Trace Elements in Soil Pore Water:
A Comparison of Sampling Methods

By

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		unit
I, II, III, IV, etc.	Oxidation state of a chemical element	
A, B	Chemical species	
(A)	Activity of species A	mol L^{-1}
[A]	Concentration of species A	defined locally
a	Activity in solution	mol L^{-1}
C_i	Concentration of the element of interest	defined locally
d	Diameter of pores	nm, µm or mm
D_{eff}	Effective diffusion coefficient	$m^2\ s^{-1}$
d_s	Particle density	g cm^{-3}
e	Void ratio	%
e^-	Electron	
E	Extraction efficiency	%
E_B	Binding energy of the electron	V
Eh	Redox potential	Volts
E_K	Kinetic energy of the electron	V
pe	Minus logarithm of the relative electron activity	
F	Faraday constant	Coulomb eq^{-1}
g	Acceleration due to the gravity	m s^{-2}
h_0	Hydraulic head	cm
$h\nu$	Photon energy	eV
ΔH_r°	Standard enthalpy of reaction	J mol^{-1}
I	Ionic strength	mol L^{-1}
k	Hydraulic conductivity	m day^{-1}
k_{eq}	Equilibrium constant of a reaction	
K°_{sp}	Solubility product	

K_A°	Thermodynamic acidity constant	
K_d°	Thermodynamic dissociation constant	
K_s	Saturated hydraulic conductivity	cm s^{-1}
K_w	Dissociation constant of water	
p_a	tension applied at a point of a column	cm water
p_c	Capillary pressure	MPa (kPa)
q	Volumetric flow rate into pore water sampler	cm^3 s^{-1}
r_m	Maximum radius of influence (porous cup)	m
R	Gas constant	kcal K^{-1} mol^{-1}
R	Distribution ratio	
R_{system}	Isotopic ratio	‰ VSMOW
s	Suction	m
S	Entropy	
T	Temperature	K or °C
V	volume	defined locally
W	weight	defined locally
Z	Ionic valence	

GREEK LETTERS

α	contact angle between a fluid and a solid matrix	
α	fitted parameter of hydraulic conductivity function	kPa^{-1}
α_{A-B}	Fractionation factor (isotopic compositions)	
$\delta^{18}O$	$^{18}O/^{16}O$ isotopic ratio	‰ VSMOW
ρ_b	Bulk Density	g cm^{-3}
ε	Porosity	%
Ψ_m	Matric Potential	kPa (or bar)
θ	Moisture content (volumetric or gravitational)	
γ	surface tension of water	mJ m^{-2}
ρ	density of water	mg m^{-3}

ω	Angular velocity	rad sec^{-1}

LETTER COMBINATIONS

Alk	Alkalinity (concentration)	mol L^{-1}
BP	Bubble Point	kPa
BSM	Basic Stern Model	
CCM	Constant Capacitance Model	
CEC	Cation Exchange Capacity	
DL	Double Layer	
DLM	Double Layer Model	
DDL	Diffuse Double Layer	
DIC	Dissolved Inorganic Carbon	mg L^{-1}
DOC	Dissolved Organic Carbon	mg L^{-1}
DW	Dry Weight	g
DWB	Dry Weight Basis	
DSS	Decision Support Systems	
EC	European Commission, or European Council	
EPA	Environment Protection Agency, USA	
FA	Fulvic Acid	
FC	Moisture content at Field Capacity	
FLM	Four Layer Model	
HA	Humic Acid	
HMM	High Molecular Mass (species)	
Hp	Hanslope soil	
IAP	Ion Activity Product	
Ic	Insch soil	
ICP	Inductively Coupled Plasma	
LMM	Low Molecular Mass (species)	
LOI	Loss On Ignition	%
OM	Organic Matter	

NESCM	Non-Electrostatic Surface Complexation Model
Np	Newport soil
PE	Polyethylene
PES	Polyethersulphone
PSA	Particle size analysis
PSD	Pore size distribution
PP	Polypropylene
PTFE	Polytetrafluorethene
PVC	Polyvinylchloride
PTE	Potentially Toxic Elements
PWP	Permanent Wilting Point
QENS	Quasi-elastic neutron scattering
RCF	Relative Centrifugal Field (centrifugation)
rpm	Rotations per minute
SB	Stoke Bardolph soil
SEM	Scanning Electron Microscopy
SI	Saturation index
SMS	Soil Moisture Samplers
TLM	Triple Layer Model
VSMOW	Vienna Standard Mean Ocean Water
WHAM	Windermere Humic Aqueous Model
XRF	X-Ray Fluorescence
XRD	X-Ray Diffractometry
XPS	X-Ray Photoelectron Spectroscopy

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"*We will walk on the land,*
We will breath of the air,
We will drink from the stream,
We will live, hold the line"
(Gabriel, 1982)

A mia madre e alla mia famiglia:

'a nuttata è passata,

sta' schiaranne 'o juorno!

Abstract

This thesis examined a range of methods for sampling soil pore water to investigate the chemistry of trace elements.

In particular, the study assessed whether Rhizon™ samplers, centrifugation, high pressure squeezing and soil suspensions in simulated pore water can be viable approaches for obtaining representative samples of equilibrated soil pore water. Results for metal solubility and speciation were interpreted in terms of both soil morphological effects on trace metal dynamics and artefacts introduced at various stages during sample preparation and handling.

The main soil used in the study was an organic-rich sandy silt from a site which has served as a sewage re-processing facility for almost a century. This soil was chosen because of its importance as a long-term repository for metal-enriched sludge applied to arable land, providing a suitable medium on which to study trace metal behaviour.

Pore waters were extracted and analysed for major and trace cations and anions, pH, Dissolved Inorganic Carbon (DIC) and Dissolved Organic Carbon (DOC) at two different temperatures (5°C and 15°C), in order to evaluate the extent of bacterial activity, organic decomposition and their consequences on solute composition, during pore water extractions. Speciation was estimated from analysis of pore water chemistry using two software packages (PHREEQCi and WHAM-VI).

Pore waters showed different ranges of concentration between the various methods. Different mechanisms and/or chemical reactions were involved during the different extractions; a range of processes was identified, mainly dominated by metal complexation by humus acids and redox reactions. Results revealed that the soil studied was able to partially buffer the free ion activities of the metal ions in pore water with increasing dilutions, but demonstrated virtually no ability to buffer DOC.

Identification of the source (i.e. location of pore space) of water extracted was also investigated using water with different isotopic composition ($^{18}O/^{16}O$). Evidence showed that centrifugation was not able to differentiate between more and less mobile water at FC conditions, rather enhancing the mixing between the two pools of water (native and labelled) by and apparent process of 'infusion'. By contrast, Rhizon samplers appeared to sample water preferentially from the more accessible pool (extra-aggregate), which proved to have a composition showing incomplete mixing with the native water. The results also suggested that mixing of the two pools was rather fast and that was almost completely attained prior to pore water extraction.

The study established that the most important factors affecting pore water chemistry during extraction are the conditions to which the samples are exposed during the extraction process. For these reasons Rhizon samplers should be used as a disposable device, and are only applicable for use in high soil moisture soil contents. In contrast, they present no 'side-effects' (providing enough equilibration time) if M^{2+} (free ion activity) were needed as opposed to M_{sol} (total metal concentration in pore water), as often required in environmental studies. Centrifugation is optimal for bulk solution studies, or when homogenisation represents a key experimental point; targeted studies are also possible. Soil squeezing is subject to severe limitations in the case of prolonged extractions of biologically active soils, due to the effects of anaerobism. Squeezing should only be used for 'fast' extractions of soils. Finally, batch extractions are well suited to studies on M^{2+} equilibria, but more studies are needed to clarify the effect of soil: solution ratio on metal and DOC solubility.

1. Introduction

1.1. Background of the project

The biogeochemical availability of trace elements accumulating in soil is of concern with respect to potential phytotoxicity, plant uptake and bioaccumulation, transport to ground or surface water and human health (Abrahams, 2002).

Soil is the medium through which these pollutants move from the land surface to groundwater. During their movement through the soil, polluting substances are subject to complex physical, chemical and biological transformations. Prediction of the extent of soil pollution, and restoration of polluted soils, requires an understanding of the processes controlling the fate of pollutants within the soil.

The nature of these processes is influenced both by the waste source as well as the soil environmental conditions, under which the elements may be released to soil solution and thereby become environmentally available.

This thesis deals with some of these processes, particularly those ascribed to the soil liquid phase and, to some extent, to its interaction with the solid phase. Individual chapters provide a more comprehensive literature review and the present introduction deals with the general ideas and theoretical background underlying the project.

1.2. Trace metals in the soil system

The literature often refers to potentially toxic elements as 'trace metals' or 'heavy metals'. It is useful to remember that the first description relates to those elements which are normally present in soils in trace amounts, defined, for example, by Mattigod *et al.*, (1981) as less than 1 mol m^{-3}. The term 'heavy metal', although generally taken to mean metals of the periodic table with atomic numbers greater than 20, but excluding the alkali metals and the

alkali earths (Tiller, 1989), or metals having specific gravities > 5g cm^{-2}, has not been uniformly defined, neither in terms of atomic weight nor specific gravity. Therefore, the term should probably be avoided (Ross, 1996). In this study, as a wider range of elements has been scrutinized, the term 'trace elements' will be used. In general, trace elements exhibit a different chemical behaviour from that of the most prevalent soil components, which are commonly lithophilic[1] metals (i.e. Na, K, Mg, Ca, Fe and Al - Krauskopf, 1995). Trace elements are mostly nonlithophilic[2] and their behaviour (chemical reactivity) in soils is not so well documented.

Amongst trace elements, Cd, Cu, Ni, Pb, and Zn are common pollutants in urban industrial soils (Dudka *et al*., 1996) and their environmental concentration has increased considerably due to human activities, such as waste disposal or utilization (see Wolt, 1994, pp. 246-250). For example, Lead (Pb) increased from pre-industrial levels of typically 0.3-0.5 ng kg^{-1} - derived from crustal dust and possible volcanic input – to around 2.5 ng kg^{-1} between 1920 and 1950 in the Antarctic environment (primarily as a result of its use as tetra-alkyl Pb as an additive to petroleum), with a clear increase to 6 ng kg^{-1} between 1950 and 1980, representing twelvefold to twentyfold increase in concentration (United Nations General Assembly, 1996). They are toxic to biota and present an indirect threat to human health from contamination of groundwater and their accumulation in food crops (Martinez and Motto, 2000).

A significant source of metal contamination of crops in the UK arises from the disposal of sewage sludge on arable land (Reilly, 1991; Alloway, 1995). Table 1.1 shows the relative natural abundance, indicative concentrations of some trace elements in soil, sludges and soil pore water (see section 1.3. for a full definition), together with typical concentrations after sludge application.

[1] Generally occurring in or with silicates, as defined by Goldshmidt' distribution of elements
[2] Siderophile, chalcophile and biophile

Table 1.1. Potentially toxic element concentrations in soils, sludges and soil pore water; 'available fraction' in soil pore water refers to the free ion forms in solution.

	Soil	Municipal Sludge	UK sludges 1982[1]	UK sludges 1991[1]	UK sludges 1999[5]	EU sludges Limits[6] 2000	Soil pore water		
Element	**mmol kg^{-1}**						**µmol L^{-1}**	**µmol L^{-1} at 10% Moisture Content**	**Available fraction x 10^{6}**
Mn[2]	8.2	7.3	-	-	-	-	-	-	-
Cr	1.0	8	2.4	1.7	-	- (19)	0.01	0.001	1
B	0.9	6	-	-	-	-	5	0.5	500
Zn	0.8	18	18	14	9	38-61 (38)	0.08	0.01	10
Be	0.7	0.07[4]	-	-	-	-	0.1	0.01	17
Ni	0.5	1.7	1.0	0.6	0.4	5.1 - 6.8 (5.1)	0.17	0.02	730
Cu	0.3	10	9.8	7.4	6	16 - 28 (16)	1	0.06	175
Co	0.1	0.2	-	-	-	-	0.08	0.008	63
As[3]	0.1	0.3	-	-	-	-	0.01	0.0013	17
Sn	0.08	0.2[4]	-	-	-	-	0.2	0.02	200
Pb	0.05	1.9	2.0	1.0	0.5	3.6 - 5.8 (3.6)	0.005	0.0005	10
Mo[3]	0.02	0.06	-	-	-	-	0.0004	0.00004	230
Cd	0.001	0.2	0.08	0.03	0.014	0.2 - 0.4 (0.09)	0.04	0.004	80
Sb	0.004	0.1[4]	-	-	-	-	-	-	-

Adapted from Wolt (1994) and references therein; [1] 50th percentile, DoE, 1993; [2]Förstner (1991) and references therein;
[3] www.liv.ac.uk/~rick/BIOL202_Web/Sewage_treatment/metals_in_slu.htm;
[4]Eriksson (2001); [5] FWR (1999), from Merrington *et al.*, (2003); [6]dry matter related, in brackets the proposed values in EC (2000b);
- (dashes) refers to 'no data'.

Large-scale application of sewage sludge to agricultural land has been undertaken for over 100 years (Heaven and Delve, 1997) and is expanding due to the need to reduce disposal at sea or *via* land fill (Sonesson *et al*., 2000; DETR, 1999). Digested sludges provide a cheap source of nitrogen and phosphorus and improve the soil through their high organic matter content (40% Dry Weight - DW). They are also however contaminated with a variety of trace elements (Sörme and Lagerkvist, 2002; Koch and Rotard, 2001, Koch *et al*., 2001).

Modern legislation provides guidelines for an economic and environmentally beneficial waste disposal strategy, including sewage sludges (EC, 2000c; MAFF, 1996; DoE, 1996). Decision support systems (DSS) for optimisation of sewage sludge application are increasingly needed (Horn *et al*., 2003).

Progressive implementation of the Urban Waste Water Treatment Directive 91/271/EEC in Europe has increased the quantities of sewage sludge requiring disposal. From an annual production of 5.5 million tonnes of dry matter in 1992, the European Community (EC) is heading towards 9 million tonnes in 2005 (Fig. 1.1, Lagenkamp and Marmo, 2000).

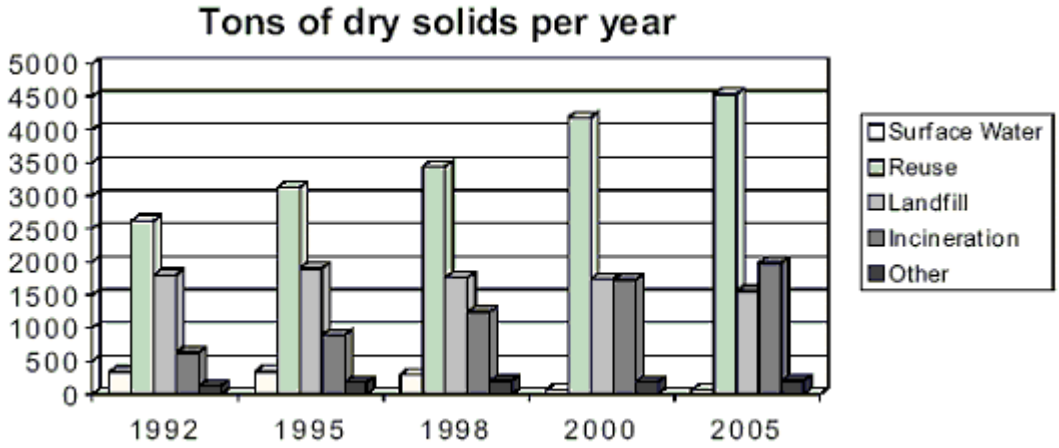


Figure 1.1. Sewage sludge production in the EU from 1992 with projection to 2005 (after Langenkamp and Marmo, 2000). Based on Urban Waste Water Treatment Directive (EC, 1991) - http://europa.eu.int/comm/environment/waste/sludge/

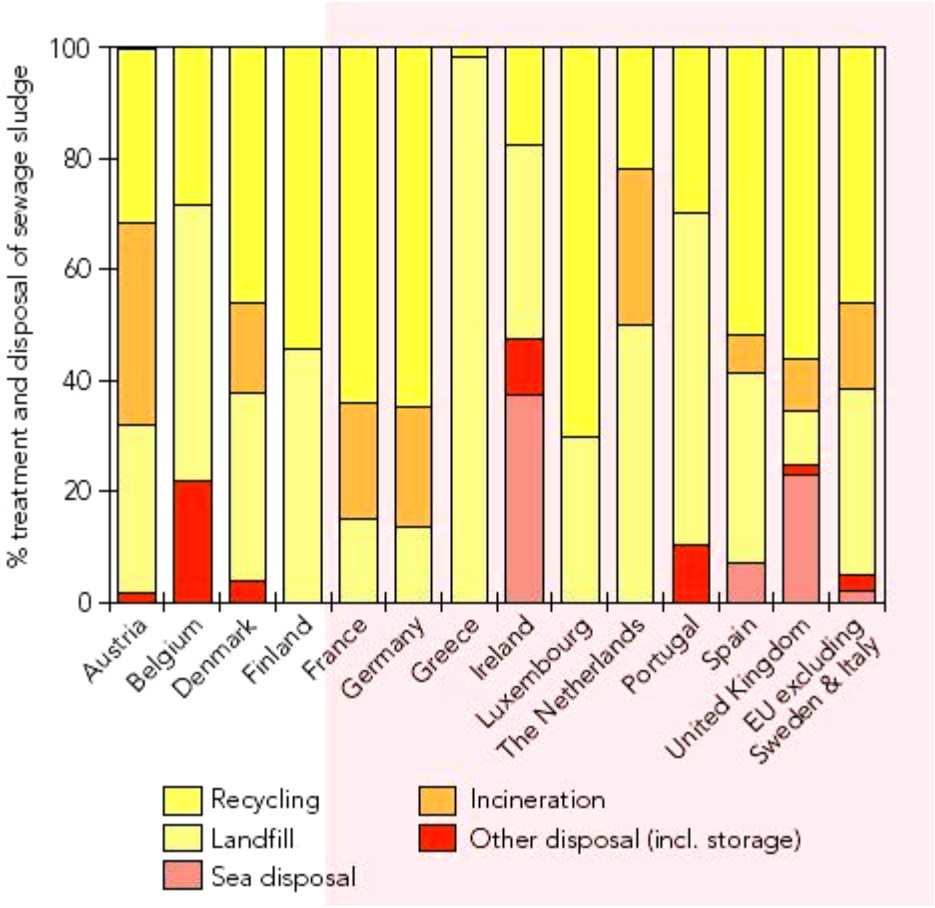


Figure 1.2. Sludge treatment: variation in EU. Source: European Commission, 1998, available online: http://reports.eea.eu.int/92-9157-202-0/en/3.7.pdf.

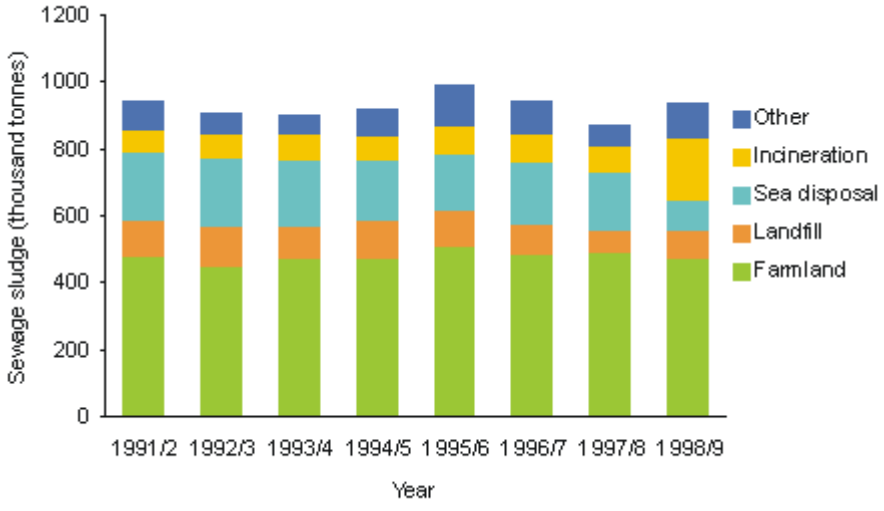


Figure 1.3. Re-use and disposal of sewage sludge in the UK between 1991 and 1999. Source: http://www.environment-agency.gov.uk/commondata/103196/waste5.

EC directive 86/278/EEC (EC, 1986) regulates application of sewage sludge to agricultural land, which is currently the preferred option for recycling (EC, 2000b). Recycling rates in the EU vary from 11% to > 50% (Fig. 1.2 and 1.3 - EC, 2000a).

In recent years, concentrations of most metals in sludges have decreased as a result of improved effluent control and waste minimisation (Alloway, 1995 – see Table 1.1). In addition, the proposals for a revision of current EU legislation suggest more restrictive limits to assure sustainable organic waste management up to 2025 (EC, 2000a,c).

The availability of agricultural land in the vicinity of wastewater treatment plants has been the primary factor determining disposal routes (particularly in the UK), resulting in a historical legacy of heavily contaminated land (Gendebien *et al*., 1999). Furthermore, in view of the very long residence periods of trace metals in most soils, it is important to be aware of the existing legacy from metals in sludges applied to land in the past. In fact, the decision to apply sewage sludge to agricultural land should be governed by a soil's ability to buffer trace metals input rather than by the general notion of sustainability. The impact of sludge application on fertility, bioavailability, plant uptake (Keefer *et al*., 1986; Bidwell and Dowdy, 1987; Gardiner *et al*., 1995; Sterret *et al*., 1996; Hooda *et al*., 1997; Miner *et al*., 1997; Hamon *et al*., 1999; Keller *et al*., 2001), fate of pollutants (Wilson *et al*., 1997; Mbila *et al*., 2001; Antoniadis and Alloway, 2002; Parkpian *et al*., 2002), general soil chemistry (Behel *et al*., 1983; Essington and Mattigod, 1991; McGrath and Cegarra, 1992; Candelaria and Chang, 1997; Hyun *et al*., 1998; Salam and Helmke, 1998; Carbonell-Barrachina *et al*., 1999; Polo *et al*., 1999;), and the effect on physical properties in soils (Logan *et al*., 1996; Sort and Alcaniz, 1999) have all been investigated.

The nature of the sludge may affect the form of retained trace metal and the degree to which that form has a controlling influence on soil reactivity. Despite numerous of studies, gaps and flaws in the understanding of the

chemistry of sludge-amended soils remain. This lack of knowledge generates a situation where national regulations for land-applied wastes restrict only 10-12 metals at most (McBride, 2003). Hence, toxic elements and organic compounds known to be present in wastes at concentrations much higher than in soils are being applied to land without regulation. For example US EPA 503 rule, which regulates loading limits to agricultural soil for 8 metals present in sewage sludge, does not impose any limits on Mo and Cr. A recent survey carried out in Canada also revealed variable and sometimes very high levels of unregulated toxic metals, including Tl, Sn, Sb and Ag (Webber and Nichols, 1995; Webber and Bedford, 1996). In the UK the list of recognised potentially toxic elements (PTE) currently includes Zn, Cu, Ni, Cd, Pb, Hg, Cr, Mo, Se, As and F (MAFF, 1998).

In summary, the ecological and human hazard of all unregulated toxic compounds is sometimes assumed to be not significant, based on the lack of evidence indicating otherwise. On the contrary, this situation should stimulate more interest and appropriate studies in order to fill the existing gap of knowledge.

1.3. Soil pore water and the concept of (bio)availability

Many studies have examined the concentration and retention of metals in soils and the effect of various parameters on their adsorption and solubility, including pH (McBride and Blasiak, 1979, Cavallaro and McBride, 1980; Harter, 1983; Robb and Young, 1999; Green *et al*., 2003), redox conditions (Davranche and Bollinger, 2001; Davranche *et al*., 2003; Qafoku *et al*., 2003), amount of metals (Garcia-Miragaya, 1984; Basta and Tabatabai, 1992; Sauvé *et al*., 2000), cation exchange capacity (Ziper *et al*., 1988), organic matter content (Gerritse and Vandriel, 1984; Elliot *et al*., 1986; Benedetti *et al*., 1996a, 1996b; Kinniburgh *et al*., 1999; Kashem and Singh, 2001), soil mineralogy (Tiller *et al*., 1963; Jenne, 1968; Kinniburgh *et al*., 1976; Cavallaro and McBride, 1984; Kuo, 1986; Lindroos *et al*., 2003), biological and microbial conditions

(Gerritse *et al*., 1992; Dumestre *et al*., 1999; Warren and Haack, 2001) as well as developing assemblage models to mechanistically predict these processes (Dzombak and Morel, 1987; Haworth, 1990; McBride *et al*., 1997; Celardin, 1999; Weng *et al*., 2002; Impellitteri *et al*., 2003, Tye *et al*., 2003 - see Chapter 4 for a comprehensive review). From these studies it has emerged that total soil metal content alone is not a good measure of short-term bioavailability and not a very useful tool to determine potential risks from soil contamination (Tack *et al*., 1995; Sauvé *et al*., 1998). In fact, since plants take up most nutrients from the soil pore water, it is often assumed that the dissolved trace metals are readily available to organisms (Barber, 1984; Vig *et al*., 2003). The definition of bioavailability (or phytoavailability) as given by Sposito (1989) suggests, "a chemical element is bioavailable if it is present as, or can be transformed readily to, the free-ion species, if it can move to plant roots on a time scale that is relevant to plant growth and development, and if, once absorbed by the root, it affects the life cycle of the plant". It is clear that the concentration and speciation of metals in the pore water may provide more useful information on metal bioavailability and toxicity than total soil concentration (Hani, 1996; Knight *et al*., 1998; Cances *et al*., 2003; Percival, 2003; Prokop *et al*., 2003; Shan *et al*., 2003). Traditionally, however, the soil pore water has not been utilized as a means of assessing bioavailability. This has probably been due analytical and technical difficulties related to sampling of the soil pore water. Instead, most assessments of metal availability have involved chemical extractants (e.g. EDTA, acetic acid) intended to remove the entire reservoir of reactive metal. This pool may involve a total amount of metal which is several orders of magnitude greater than that found in the soil pore water.

1.3.1. Soil pore water definition

The soil liquid phase has a composition and reactivity defined by the properties of the incoming water and fluxes of matter and energy originating

from the local (neighbouring) soil solid phase, biological system, and atmosphere (Fig. 1.4).

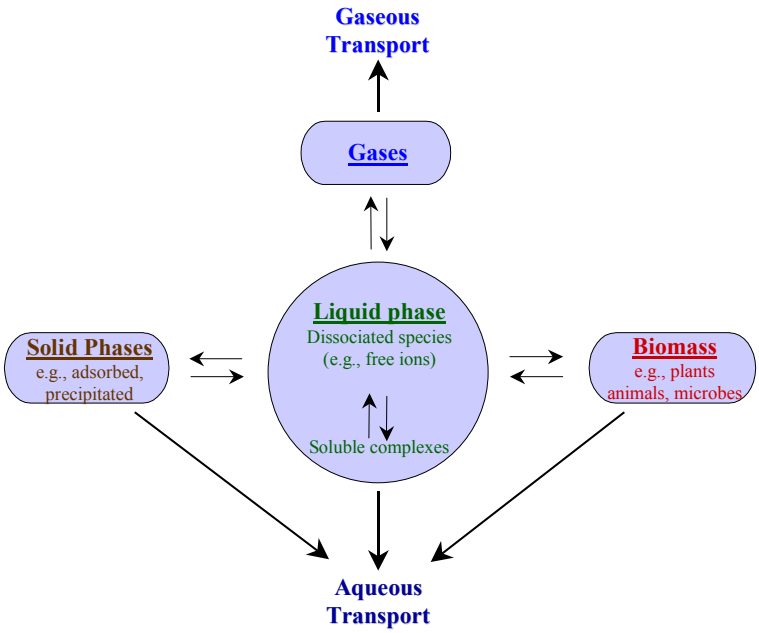


Figure 1.4. Biogeochemical cycling of soil contaminants: the soil liquid phase is acting as a regulator of contaminant fate (modified, from Hesterberg, 1998, based on Lindsay, 1979; Mattigod *et al.*, 1981).

The current view is that in a porous medium, two liquid-phase regions can be identified on functional grounds (Yaron *et al.*, 1996). The first is near the solid phase and is considered the most important surface reaction zone of the porous medium system. This near-surface water also controls the diffusion of the mobile fraction of the solute in contact with (sorbed on) the solid phase. The second region covers the 'free' water zone, which governs the water flow and solute transport in soils (Fig. 1.5. - for a definition of water states, see Chapter 2).

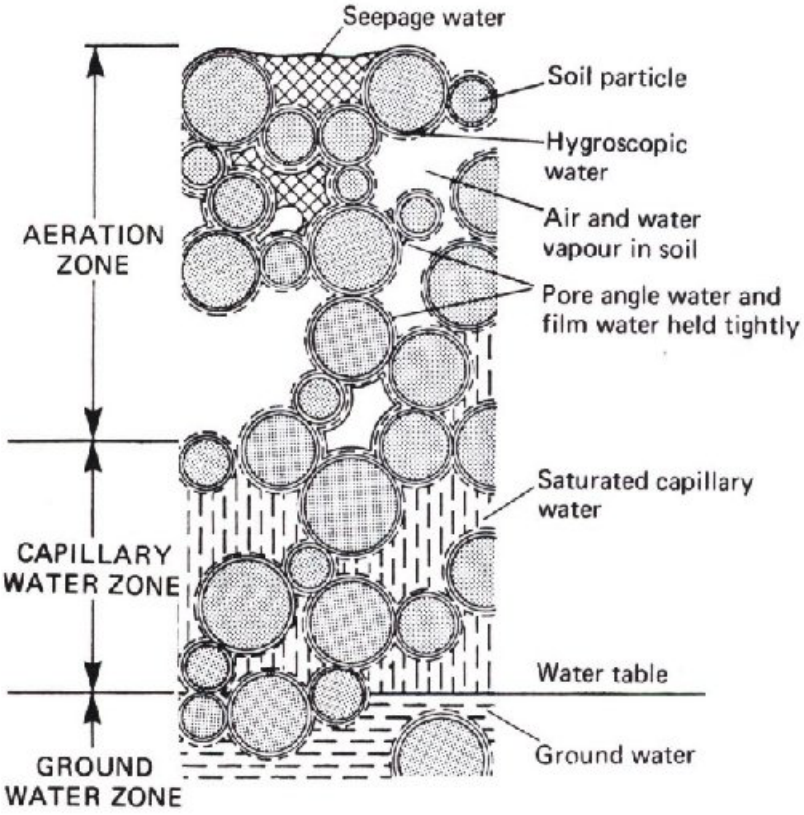


Figure 1.5. Schematic representation of soil water states and their definitions (from Shaw, 1993).

Both phases represent what can be defined as 'soil pore water': this term is preferred to the more specific 'soil solution' and will be use throughout this thesis.

1.3.2. Bioavailability and soil pore water sampling

To assess the environmental bioavailability, mobility and geochemical cycling of trace elements in soil, analyses of soil pore water composition are frequently more instructive than those from whole soil or soil extracts. The validity of this concept has led to the development of several models that attempt to predict solid solution partitioning of elements and their solution speciation. These 'assemblage models' include an increasing number of variables as they develop greater mechanistic capability. Soil pore water

analysis can be used to model the nature, direction, extent, and rate of chemical reactions. In fact we can assume that:

1. if soil pore water represents the natural medium for plant growth, then soil pore water analysis allows for prediction of plant response to chemicals occurring in the soil environment (plant uptake prediction);
2. if soil pore water can be related to mobile water in the soil environment, then soil pore water composition can be used to predict the forms and amounts of chemical that may reach ground and surface water through transport from the soil environment (pollutant fate);
3. if soil pore water approaches a steady state relative to the soil solid phase, then soil pore water composition can be used to predict solid phase components controlling chemical distribution in soil (solid-solution processes).

The validity of these assumptions depends on the way that soil pore water is conceptualised, i.e. defined and sampled, and how that concept is translated into an operational method or model whereby soil pore water can be obtained and its composition expressed in a meaningful way. Too often, however, studies skim over a proper definition of soil pore water opting for 'simulating' or bypassing the problem.

A range of methods are available for obtaining and analysing 'unaltered' soil pore water, with consideration of ion speciation and complexation, and expression of soil pore water composition in thermodynamic terms (see Chapter 3 and 4). Unfortunately, none of them has been adopted as 'the standard procedure', leading to a rather confused situation.

Sampling of soil pore water often presents conceptual ambiguity as well as technical problems, especially if one tries to characterize the liquid phase in terms of its origin within the soil system. In fact, soil porosity generally represents a limiting factor in defining the ratio between the solid, aqueous and gaseous phases of the soil medium (Yaron *et al.*, 1996) due to the open

boundaries between these different phases leading to a pattern of continuously changing processes. In addition, solute concentrations in sampled soil solution may depend on a number of technical factors, including,

- method of extraction,
- imposed tensions,
- flow rate to the sampler,
- relation of the soil volume sampled versus the scale of heterogeneity in solute concentration (scaling factor).

This situation is made even more complicated by the wide range of methods of pore water extraction used (see Reeder *et al.*, 1998). Solute concentrations have rarely been measured across a range of pore size and examined in relation to soil physical properties such as the effective pore size distribution or the water retention characteristics of the soil. Such a comparison would be facilitated by an improved methodology to sample solute concentration in relation to pore size (Harvey, 1993).

1.4. Objectives of project

The aim of this project is to investigate methods for sampling soil pore water to interpret differences between methods and examine whether there is any effect of pore size and heterogeneity on observed trace element concentrations. Relevant soil characteristics are included in the evaluation of chemical heterogeneity of trace metals concentrations in soil pore water to determine the extent and possible sources that lead to these heterogeneities.

Identification of the source (in terms of location in the pore space) of water collected and the meaning of the resulting trace metal concentrations is questioned. The hypothesis that incomplete mixing of soil water between large and small pore networks occurs, which may significantly affect solute travel time and chemical transformation as water and solute pass through soil (reviewed by Nielsen *et al.*, 1986; see also White, 1985) is tested.

According to Tyler (2000) a stable ionic/elemental equilibrium is not likely to be attained in the entire soil pore water of any type of soil. Pore water contained in micropores, isolated aggregates, within clay lattices, etc. are only in contact with solution in the macropores to a limited extent. The spatial variability of microbial activity constitutes an additional factor to the heterogeneous nature of these processes and the possibility of isolated microenvironments within a soil.

1.4.1 Structure of the thesis

To address the issues identified here, the thesis is organized as follows:

In **Chapter 2** the soil studied is characterised for the parameters already known to be fundamental, such as pH, cation exchange capacity, organic matter content, mineralogy, together with physical properties such as pore size distribution, water retention and particle size.

In **Chapter 3**, the methods of soil pore water extraction currently available are reviewed (**Rhizon samplers, centrifugation**) and compared with a methodology never previously used for soils (**pressure filtering**).

In **Chapter 4,** following on from the need to establish how the composition of soil pore water differ according to the method of collection, and the extent to which these differences reflect the histories of the pore water, an experiment is undertaken in order to extract soil pore water in a systematic way across a range of pressures (pore sizes) and to assess their variation in chemical composition and speciation.

In **Chapter 5**, a batch experiment is carried out to study the effect of varying soil:solution ratios on the metal buffer capacity of the soil studied and to assess the validity of methods of soil pore water sampling such as water extracts (suspensions or pastes) and leaching.

In **Chapter 6**, two of the extraction methodologies employed in the thesis (Rhizon samplers and centrifugation) are studied using ^{18}O as a tracer to account for their efficiency in targeting water from a definite range of pores,

but also to assess how water travels between the pores of a sample during sample pre-treatment and soil pore water extraction.

In **Chapter 7**, a summary of all the major findings is given, together with a discussion of the advantages and disadvantages of the approach employed and final recommendations on soil pore water sampling.

In summary, this project focuses on soil pore water, its extraction and composition, attempting to define whether this is actually representative of the 'true' conditions in a soil system or whether artefacts are introduced at various stages during sample preparation and handling.

2. Soil physical and chemical properties affecting the distribution of trace metals

2.1. Introduction

This chapter examines properties of the soil solid and liquid phases relevant to this study. In particular, soil pore water will be considered, together with soil characteristics that generally determine its magnitude and composition, specifically,

- Texture (Particle size analysis – PSA)
- Bulk density and porosity
- Pore size distribution (Moisture release curve)
- pH
- Organic Matter content (Loss on Ignition – LOI)
- Cation Exchange Capacity (CEC)
- Total metal content (X-Ray Fluorescence – XRF)
- Mineral composition (X-Ray Diffractometry – XRD)
- Surface composition and speciation (X-Ray Photoelectron Spectroscopy – XPS; Scanning Electron Microscopy – SEM)

Aspects of soil pre-treatment and incubation conditions prior to solution sampling, such as moisture content and residence time (equilibration time), storage conditions (temperature), homogeneity, will be considered.

2.2. Soil sampling and storage

Soil samples are generally air-dried (sometimes freeze-dried) upon return in the laboratory, sieved (< 2 mm or fine earth fraction), homogenized, and stored prior to analysis. Although some soil chemical characteristics may change in the drying process this is generally preferred over working with field-moist samples because of the difficulties of homogenising samples and

halt microbial processes. In this study, however, the importance of preserving the natural moisture and chemical conditions of the soil prevailed over some of the possible drawbacks that can arise while working with wet samples. Several studies indicate that this is a suitable approach rather than drying and re-wetting samples, especially when pore water has to be extracted from the soil (Jones and Edwards, 1993; Curtin and Smillie, 1995, Chapman *et al*., 1997b; Bordas and Bourg, 1998; Gray and McLaren, 2003; Perez *et al*., 2004).

2.3. Water retention and soil porosity

2.3.1. Physical state of water in soils

Within the soil system, storage of water is influenced by several different forces. The strongest force is molecular, resulting from close association with the surface of soil minerals. Water retained by this force is termed *hygroscopic water* and consists of films of water held within 0.0002 mm of the surface of soil particles (Fig. 2.1). Hygroscopic water is essentially non-mobile and can only be removed from the soil through heating or freeze-drying. The matric force holds soil water between 0.0002 to 0.06 mm from the surface of soil particles. This force is due to two processes: soil particle surface molecular attraction (*adhesion* and *absorption*) to water and the cohesion that water molecules have to each other. This force declines in strength with distance from the soil particle and becomes negligible past 0.06 mm. *Capillary action* moves water from areas where the matric force is low to areas where it is high, hence such water is often termed *capillary water*. Capillary water can be removed by air-drying or by plant uptake, but cannot be removed by gravity. Plants extract this water through their roots until the soil capillary force (force holding water within the soil) is equal to the extractive force of the plant root. Plants can use most of this water by way of capillary action until the soil *wilting point* is reached.

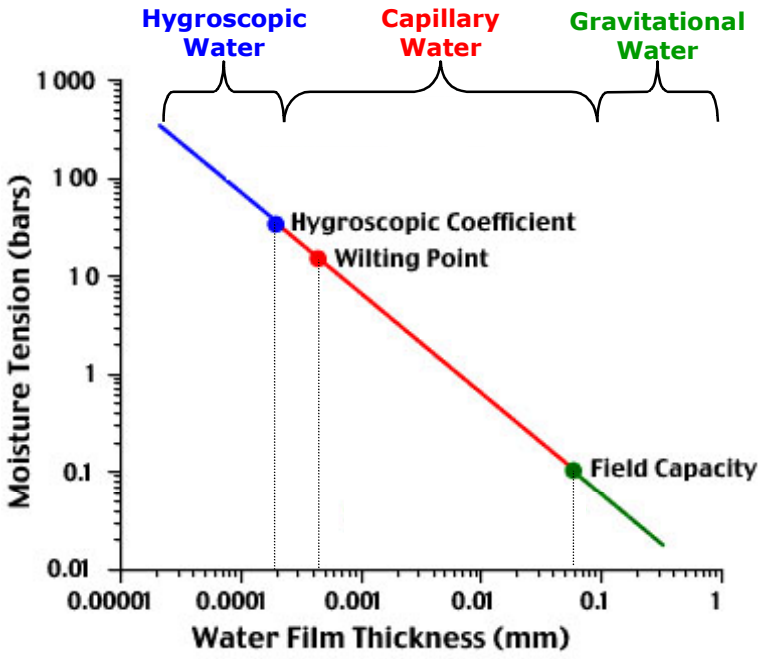


Figure 2.1. Relationship between soil water film thickness and moisture tension; force is measured in bars (1 bar = 100 kPa) (modified, from http://www.physicalgeography.net, created by Micheal Pidwirny).

Water in excess of capillary and hygroscopic water is called *gravitational water*. Gravitational water is found greater than 0.06 mm from the surface of soil particles and it moves freely under the effect of gravity. When gravitational water has drained away the amount of water that remains defines the soil's *Field Capacity* (FC). Figure 2.1 illustrates the relationship between the thickness of water film around soil particles and the magnitude of the force that holds this water. The amount of water in the soil is controlled by the soil texture and porosity. Soils dominated by clay-sized particles have more pore space (*per* unit volume) than soils dominated by sand. As a result, fine-grained soils have higher field capacities than coarse-grained soils.

2.3.2. Porosity and pore size distribution

Pores in soils range in size over several orders of magnitude, reflected by resulting porosity (or by the void ratio), illustrated by examples in Table 2.1 (see also Table 2.2).

Table 2.1. Examples of the range of values of bulk density and associated properties for selected soils. Particle density is taken as 2.65 g cm^{-3}.

Description	Bulk Density, ρ_b g cm^{-3}	Porosity, ε	Void ratio, e
Surface soil of wet clay	1.12	0.58	1.37
Surface soil of loam texture	1.28	0.52	1.07
Spheres of uniform size in open packing	1.39	0.48	0.91
Subsoil of sandy texture	1.61	0.39	0.65
Sandy loam compacted by heavy traffic	1.90	0.28	0.39
Spheres of uniform size in closest packing	1.96	0.26	0.35
Sandstone	2.12	0.20	0.25

Source: Marshall and Holmes, 1979.

Pores size is important since they take part in a variety of processes and functions (see Table 2.2). Numerous studies attempt to categorize soil pores within defined physical frames; some of them are given in Table 2.2, but many more examples can be found in the literature (Jongerius, 1957; Marshall, 1959; Bullock and Thomasson, 1979; Beven and Germann, 1982). This study adopts the classification proposed by Greenland and Hayes (1981) because it links functional arrangement of pore size to plant-water interaction. In this way it provides a general idea of the impact of soil pore dimensions on the water and solute status in the soil medium (Table 2.2). In this classification pores are subdivided as:

1. **Transmission pores** (> 50 μm equivalent cylindrical diameter) - hold excess water that is free to drain, between (and sometimes within) aggregates. These pores enable soil to drain after rain or flooding, and are then filled with air. The movement of gases through transmission

pores is essential for the proliferation of aerobic microorganisms and respiration of the plant root system.

2. **Storage pores** (ranging from 0.5 µm to 50 µm diameter). These retain water against the force of gravity, but allow water uptake by plant roots.
3. **Residual pores** (< 0.5 µm diameter). These retain water against the forces of gravity and those exerted by plant roots

The extent of storage and residual pores depends on the composition and the amounts of the solid components present in the aggregates.

2.3.2.1. Moisture Characteristic

Water content is usually measured by determining the loss of mass, m_w, on drying in an oven to a constant mass, m_s, at the arbitrary temperature of 105 °C. Water content, as a volume fraction, ranges from zero at oven dryness to a value ε at pore space saturation. Two intermediate stages are commonly recognised during the drying of wet soil. *Field capacity*, is the water content found when a thoroughly wetted soil has drained for approximately two days (or until further drainage is negligible). ***Permanent wilting point*** is the lowest water content that can be reached in the soil due to plant extraction. Both tend to increase with increasing clay content in the soil, however, the size distribution of pores influences water retention, water movement and aeration more than the size distribution of particle (Marshall and Holmes, 1979).

Matric potential, Ψ_m, is a pressure potential that arises from the interaction of water with the matrix of solid particles in which it is embedded. There are various methods to determine matric potential, which together enable the full range from wet to dry to be covered.

Table 2.2. Examples of soil pore classifications, with description of equivalent soil water phenomena and matric pressures; a brief illustration of the soil system in those conditions is also given; 'd' represents the equivalent diameter of pores and is expressed in µm, unless otherwise stated.

Size (m)	**Soil system**	**Functional classification (µm)**	**Physical classification**		**Predominant water phenomena**	**Size (µm)**	**†Equivalent water pressure (kPa)**
		Greenland and Hayes, 1981	*Brewer, 1964*	*Luxmoore, 1981*			
10^{-2}	Spaces as large as these are commonly formed between the clods of newly ploughed soil. Cracks in dry clay soils can reach widths of this order of magnitude.	**Transmission pores**: air movement and drainage of excess water d > 50	Macropores d > 1000	Macropores d > 1000	Channel flow through profile from surface ponding and/or perched water table	10000	- 0.015
10^{-3} (1 mm)	Pores of about this size and smaller are formed between aggregates of finely tilled soil as for a seed-bed.		Fine Macropores 75 < d < 1000	Mesopores 10 < d < 1000	Drainage; hysteresis; gravitational driving force for water dynamics	1000	- 0.15
10^{-4}	Pores between spherical particles 0.65 mm in diameter in closest packing have this size (Dallavalle, 1948). Roots will not extend into rigid pores smaller than this (Wiersum, 1957).	**Storage pores**: retention of water against gravity and release to plant roots 0.5 < d < 50				100	- 1.5
10^{-5}	Pores larger than about 15 µm (corresponding to 9.8 kPa) are drained in most soils that can be said to be at Field Capacity.		Mesopores 30 < d < 75	Micropores d < 10	Evapotranspiration; matric pressure gradient for water distribution	10	- 15
10^{-6} (1 µm)	Pores down to this size are accessible to bacteria.		Micropores d < 30 (< 0.5)	**Physico-Chemical classification (adsorption)** *IUPAC, 2001*		1	- 150
10^{-7}	Water in pores of about this size or larger is available to plants in non-saline soil (correspond to 1500 kPa).	**Residual pores**: retention and diffusion of ions in solution 0.005 < d < 0.5	Ultramicropores 0.5 < d < 0.1	Macropores d > 0.05	Capillary condensation; transport	0.1	- 1500 (**PWP#**)
10^{-8}	When micropores are treated as slits between parallel plates, about half the pore space in dried aggregates of clay soil can commonly be attributed to plate separations of 10 nm or less (Sills *et al.*, 1974).			Mesopores 0.002 < d < 0.05		0.01	- 15000*
10^{-9} (1 nm)	Roughly corresponding to the thickness of 3 layers of water molecules on a clay surface.	**Bonding spaces**: support major forces between soil particles d < 0.005	Cryptopores d < 0.1	Micropores d < 0.002	Physisorption; adsorbate-adsorbate and adsorbant-adsorbate interactions	0.001	- 150000*

†Calculated using equation (2.1); # PWP = Permanent Wilting Point.

*These values are only indicatives: a different equation should be used above the PWP, and the relative vapour pressure of the soil water included

The relation between water content, θ, and matric potential (or suction), Ψ_m, is a basic property of a soil, called the ***moisture characteristic*** (also *water retentivity curve* or *water characteristic function*). The moisture characteristic is constructed by measuring θ with change in tension placed on soil on progressively drying soils. The 'tension' imposed is equivalent to the value of Ψ_m counteracting the applied tension. The tension is also inversely related to the soil pore radius of the largest pores holding water at that tension, when soil shrinking is negligible with drying. An effective size of pore can be calculated from the suction using equation (2.1),

$$p = -\rho g s = -\frac{2\gamma \cos\alpha}{r} \qquad (2.1)$$

where: p is the pressure of the water, γ is the surface tension of water (72.75 mJ m^{-2} at 20°C), r is the tube or pore radius, ρ is the density of water (0.9982 mg m^{-3} at 20°C), g is the acceleration due to the gravity (9.80 m s^{-2}), s (in m) is the suction and α is the contact angle, which is normally to be zero. On this basis, a moisture characteristic can be used to show the amount of pore space (as given by the water content on a volume basis) consisting of pores smaller than a given effective size (Fig. 2.2).

The benefit of using pore size ranges to classify soil water (see Table 2.2) is the ability to distinguish *micro-* and *mesopore* capillary water (subject to diffusive flow through the soil profile) from non-capillary *macropore* water (that contributes to channelised or bypass flow in soils).

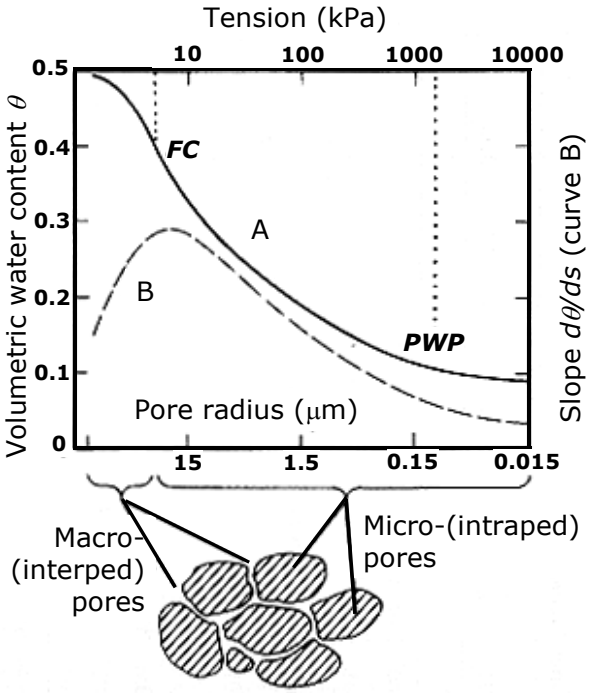


Figure 2.2. Idealised graphs of (A) the water characteristic function and (B) specific water-holding capacity for a clay soil (modified, from White, 1987); FC = Field Capacity; PWP = Permanent Wilting Point.

2.4. Nature and properties of the soil solid phase

The majority of chemical interactions in soil take place at the particle–solution interface (Bolt *et al.*, 1991). The nature and properties of soil particles therefore have a controlling influence on important soil processes. The expression of these properties depends on the composition of soil particle surfaces. For many soils, this composition is likely to differ from that of the bulk material since soil particles commonly have a covering of extraneous substances. For example, humified organic matter (OM) complexed with polyvalent cations and Fe/Al/Mn hydrous oxides are known to form coatings around soil particles and a lining within aggregate pores (De Coninck, 1980). These constituents have also been identified as the primary reservoirs of metals in soil and sediments. The chemical composition of such coatings and other cementing agents has been extensively studied using various techniques, including selective dissolution, optical microscopy (X-ray

diffraction – XRD), scanning electron microscopy, and energy dispersive X-ray analysis (SEM-EDX) (McKeague and Wang, 1980; McHardy and Robertson, 1983; Courchesne *et al*., 1996). Although usually qualitative, and often not sensitive enough to detect forms present in very small amounts (Mattigod *et al*., 1986; Essington and Mattigod, 1991), these methods provide useful knowledge about the nature of the soil constituent involved, so that the various chemical forms present can be more precisely characterized (Adamo *et al*., 1996). Each of the se 'conventional' analytical techniques has limitations by being either invasive, incapable of detecting certain constituent elements, or not being surface-specific. *X-ray photoelectron spectroscopy* (*XPS*) or electron spectroscopy for chemical analysis (ESCA) has none of these limitations.

2.4.1. Surface analyses by X-ray photoelectron spectroscopy

XPS can be used for analysis of the elemental composition of particle surfaces and in heavy metals adsorption studies, e.g. Gier and Johns (2000), Yuan *et al*. (1998). XPS has the advantage of being able to detect all elements in soil except for H and He. The principal advantage of XPS however is its surface specificity in that the 'depth' of analysis only extends to several nanometres from the particle surface (Briggs and Seah, 1990). It is also able to yield information on chemical specificity, i.e. the ability to identify not only the elements present in the analysis, but also their chemical state. In the case of iron, for instance, the spectra of Fe^{0}, Fe^{2+}, and Fe^{3+} are all distinguishable; in the case of carbon it is possible to separate the hydrocarbon and non-hydrocarbon (e.g., carbonyl group, see Fig. 2.3). Various data sets exist that catalogue XPS chemical shift.

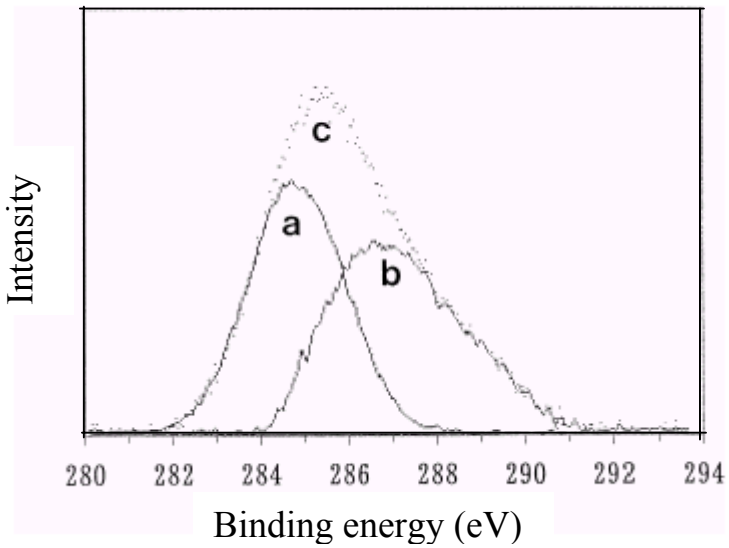


Figure 2.3. Observed C(1s) spectrum 'c' of a soil with computer fit components 'a' and 'b'. Bands 'a' and 'b' indicate C(1s) spectra due to hydrocarbon and non-hydrocarbon (e.g., carbonyl group), respectively (from Yuan *et al.*, 1998).

XPS has rarely been applied to probe the surface composition of soil particles. However it has the potential to assess the chemical composition of soil particle surfaces of contaminated soils, especially when formation, translocation, and deposition of amorphous materials within the soil profile occur, all of which are surface-controlled processes.

2.5. Materials and methods

2.5.1. Soil sampling and preparation

The soil chosen for this investigation was sampled at a sewage re-processing facility ('sewage farm'), run by Severn Trent Water at Stoke Bardolph near Nottingham, England (GR: SK643 406). The farm is approximately 700 ha, with about 60 fields. The site is managed within the guidelines governing 'dedicated sites' set out by the 1989 Sludge Regulations (HMSO, 1989), and is utilised for dairying and production of livestock feed. Sewage sludge has been applied to parts of this land for approximately 100 years. The soil chosen was from a field originally used as a lagoon for sludge de-watering (Fig. 2.4). Sewage sludge is currently applied to fields via sub-

surface injection from tractor-mounted equipment, and towed pumps (Heaven and Delve, 1997).

A rigorous liming regime is followed at the site. A subset of samples analysed during a previous study for bicarbonate-extractable P (Young *et al.*, 2000), found values in the range 141-200 mg P kg^{-1} (index 7 of MAFF, 1994). An intensive geochemical survey of the farm is conducted at five yearly intervals. This involves collecting soil from 0 - 25 and 25 - 50 cm horizons and analysing for a wide range of metals and metalloids (Heaven and Delve, 1997). These data show that the sampling site chosen for this study has amongst the highest concentrations of metals, particularly Cd, from the entire site (Table 2.3; Fig. 2.5).

Figure 2.4. View of test field; the old lagoon boundary and a ring main outlet for sludge disposal are visible (from Maxted, 2003).

Table 2.3. Range of metal concentrations found within the test field and across the entire Stoke Bardolph site.

Heavy metal	Range occurring across site[1] (n = 475) (mg kg^{-1})	Range occurring in test field[1] (n = 8) (mg kg^{-1})	Maximum permissible concentrations in 'normal' agricultural soil (pH 6.0 - 7.0) [2] (mg kg^{-1})
Cd	0.2 - 75	46 - 71	3
Cu	15.6 - 1120	855 - 1011	135
Pb	26 - 870	696 - 774	300
Ni	10 - 630	499 - 591	75
Zn	82 - 2700	2129 - 2516	300

[1]Heaven and Delve (1997).
[2]The 1989 Sludge Regulations (HMSO, 1989).

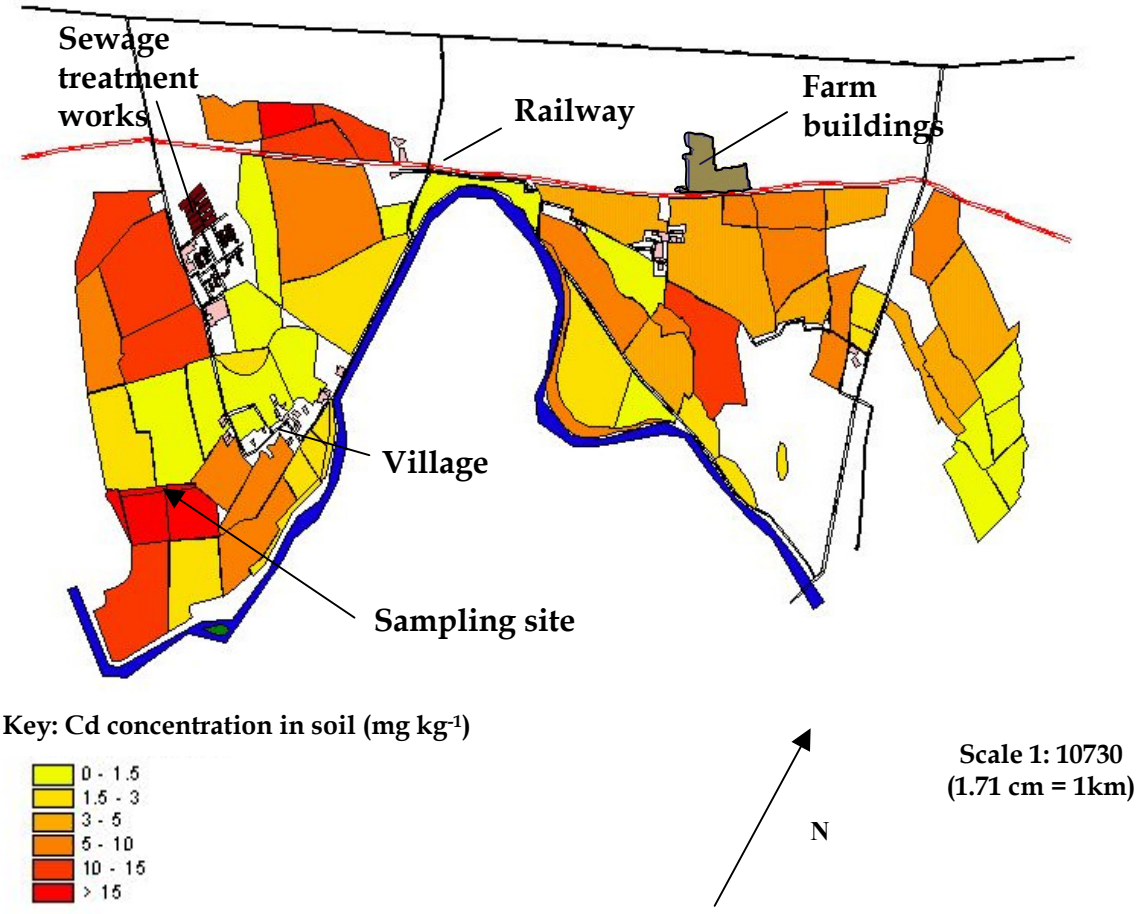


Figure 2.5. Geochemical map of the Stoke Bardolph estate illustrating the mean Cd concentration of soil (0 - 25 cm), based on field averages (Heaven and Delve, 1997). The test field is indicated (from Hough, 2003).

In addition to the principal study soil (SB), three more soils were used for comparison or cross-checking. Details of the soils are given in Table 2.4.

Table 2.4. Description of soils used in this study.

Name site	OS Ref	Soil classification	Land use	Parent material	Code
Newport	SJ 747 189	Brown sand	Arable	Glacial drift over Triassic Sandstone (Sherwood sst)	Np
Insch	NJ 650 263	Typical brown earth	Arable	Gabbro intrusion	Ic
Hanslope	TL 344 634	Calcareous pelosol	Arable	Great Oolite Series (Jurassic)	Hp
Stoke Bardolph	SK 643 406	'Sewage farm'	Sewage sludge application	Silty river alluvium over Triassic (Mercia Mudstone Group)	SB

Following sampling, field-moist soil samples were passed through a polypropylene sieve (mesh size 2 mm), thoroughly mixed and separated into two portions of 2.5 kg (dry weight basis, DWB) each; these were kept aerated and incubated at 5°C and 15°C. Moisture content was monitored on a regular basis and maintained at FC (53% gravimetric moisture content DWB - determined by suction tables), by addition of de-ionized water.

2.5.2. Physical properties

2.5.2.1. Bulk density, particle density and porosity

Soil bulk density (ρ_b), i.e. the ratio of the mass of dry solids to the bulk volume of the soil, was measured as described in Rowell (1994). Samples of the soils at FC were placed, in triplicate, in a cylindrical sampler of known mass and volume. Samples were weighed wet, prior to drying at 105°C for 24 h and then re-weighed. Bulk density was expressed in g cm^{-3}.

Particle density (d_s), i.e. the ratio of the total mass of the solid particles to their total volume (excluding pore spaces between particles), was measured

as described in Rowell (1994). A volume of 25 cm^3 of dry soil (< 2mm) was placed in a weighed 250 ml beaker and re-weighed (*a*, dry soil). De-ionised water (50 cm^3) was then added and boiled gently to disperse the soil and eliminate air. The beaker was cooled in running water, its contents were placed in a weighed 250 ml flask and weighed (*b*, wet soil). Particle density (d_s) was then calculated as follows:

$$d_s = \frac{M_s}{V_s} \tag{2.2}$$

where $V_s = V_{flask} - V_{H_2O}$; $V_{H_2O} = \frac{b-a}{d_{H_2O}}$

and M_s is the mass of dry soil.

Porosity was calculated from the measured values of bulk and particle density:

$$\varepsilon = 1 - \left(\frac{\rho_b}{d_s} \right) \tag{2.3}$$

2.5.2.2. Particle size distribution

Particle size distribution was measured with a Beckman Coulter LS 230, using the principle of laser diffraction. A sample placed in a fluid module is circulated through a sample cell at a constant speed. A beam of laser light shone through the cell is diffracted by particles within the sample, and the forward scattered (or diffracted) light is collected by a series of collectors. The distribution of light falling on the sensors enables the size distribution of the sample to be calculated. This method enables the measurement of particles from 0.4 µm to 2000 µm (0.0004 mm to 2 mm).

A sample of 25 g of soil was treated with 30% hydrogen peroxide (H_2O_2) in order to remove organic matter. Fine samples were then adequately

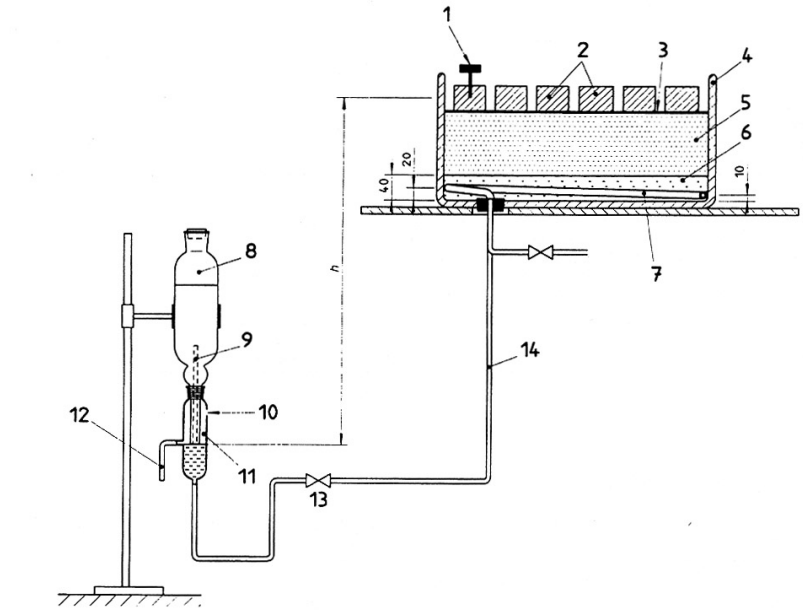
dispersed prior to analysis in order to obtain a representative particle size distribution (Head, 1992). The exact type and strength of dispersant used depends upon the nature of the sample. A 5% *Calgon* solution (recommended for soils and geological samples) was prepared by adding 35 g sodium hexametaphosphate and 7 g sodium carbonate to 1 L of distilled water (Head, 1992). A known amount of sample after H_2O_2 treatment (from few hundred mg for very fine samples, to 1-2 g for coarse-texured samples), representative of the sampled material and in stable form, was then dispersed in *Calgon* to ensure proper wetting and prevent agglomeration. Samples were stored in air-tight 250 ml nalgene bottles and placed in an ultrasonic bath for 10 min; this improves dispersion especially if the sample has been heat-treated or ashed. Samples of the soil suspension were therefore loaded directly into the fluid module, taking care not to introduce bubbles into the suspension chamber. Bubbles are caused by the degassing of water as its temperature rises and may represent a problem for this kind of methodology. Bubbles (usually in the range off 100 - 500 µm) appearing during the analysis can affect the accuracy of particle size distribution' results and should therefore be minimized.

The standard 'optical model' used for these analyses is called Fraunhofer and describes the diffraction of light by small particles. This predicts that when light from a laser is shone at a particle, some of it is diffracted. The amount of diffraction is dependent upon the size of the particle. The smaller is the particle, the greater is the maximum angle of diffraction. Thus, particles of different sizes each produce a characteristic diffraction pattern. Results show the distribution of particles in the measured size range (0.4 - 2000 µm) within the volume of sample analysed. The output also reports a parameter called ***obscuration*** (%). This represents a measure of the degree of interference within the sample cell after sample addition, i.e. the amount of sample dispersed in the cell as the relative amount of light is scattered or adsorbed by the particles, therefore indicating the attenuation of the laser

light beam caused by the sample. Obscuration must be balanced and should fall ideally between 8 and 12% for the range of particle size considered.

2.5.2.3. Soil water release curve and pore size distribution

The relationship between water content and potential, the moisture characteristic, was determined following the method described in ISO 11274 (1998). Sand and kaolin suction tables (from -5 kPa to –30 kPa) were used, together with pressurised gas and pressure membrane cells (from -100 kPa to –1500 kPa). The results obtained provide an assessment of the equivalent pore size distribution (e.g. identification of macro- and micropores) as well as indices of plant-available water in the soil (ISO 11274, 1998).



Key

1 Tensiometer in "dummy sample"
2 Soil core sample
3 Nylon voile
4 Ceramic sink
5 Fine sand (60-100 µm)
6 Coarse sand
7 Drain system
8 250 cm^3 reservoir
9 Thin nylon tube
10 Air inlet
11 Levelling bottle
12 Overflow (B)
13 Tap A
14 Flexible 7 mm id nylon tubing

Figure 2.6. Example of sand suction table (after ISO 11274, 1998); dimensions in mm.

The principle of the sand and kaolin baths relies on the application of a negative matric pressure to coarse silt or very fine sand held in a rigid watertight container (a ceramic sink or a plastic box – see Fig. 2.6). Soil samples at FC are placed in contact with the surface of the table and the application of suction causes the samples to lose pore water until their matric pressure is equivalent to that of the suction table. Equilibrium status was determined by weighing samples on a regular basis and soil water content by weighing, oven drying and reweighing.

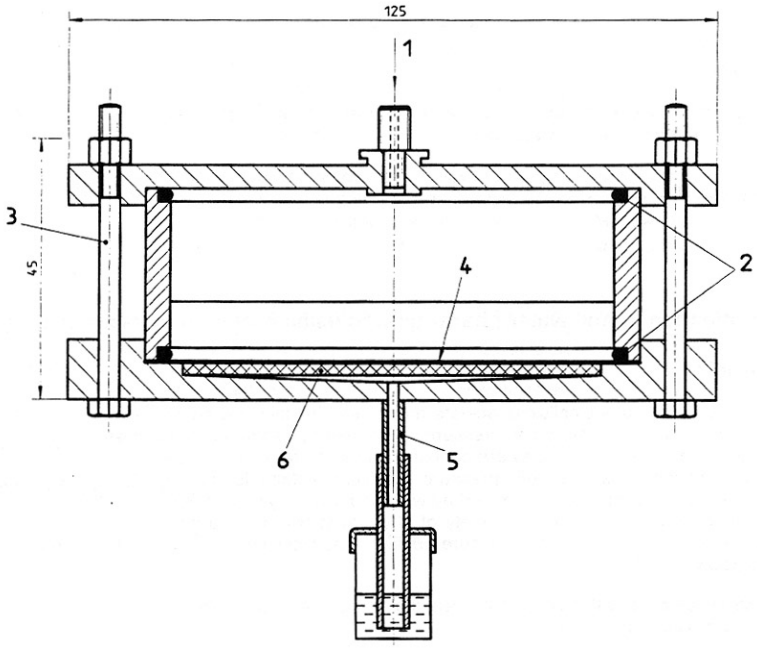


Figure 2.7. Pressure membrane cell (after ISO 11274, 1998); dimensions in mm.

During the use of the pressure membrane cells soils were placed on a porous acetate membrane, and brought to equilibrium at a given matric pressure p_m by applying a positive gas pressure p; the matric pressure of the samples equals $-p$. To maintain this pressure, the membrane and samples are contained within a pressure chamber (Fig. 2.7), whilst the underside of the

porous medium is maintained at atmospheric pressure. Equilibrium status was judged to be attained when water outflow from the cell ceased and soil water content was determined as described for the sand bath (ISO 11274, 1998).

2.5.3. Chemical properties

A pH, Cation Exchange Capacity (CEC) and organic carbon content by Loss on Ignition (LOI), were measured on the soil studied.

2.5.3.1. pH

The pH of each soil was determined (Rowell, 1994) using a combined glass electrode (AgCl) with an Orion 720A meter. Soil (10 g, <2mm) was suspended in 25 ml of de-ionised water, samples were magnetically stirred for one minute and then left to settle for 15 minutes. Prior to recording the pH value the samples were stirred to reform the suspension.

2.5.3.2. Cation Exchange Capacity (CEC)

The technique used was based on compulsive exchange between an aqueous solution of magnesium sulphate and a barium-saturated soil. Exchange sites were saturated with barium, supplied as a 1:1 barium chloride/triethanolamine solution buffered at pH 8.10, and any excess was removed by washing. Magnesium sulphate solution was added, barium was precipitated as insoluble barium sulphate, and the magnesium adsorbed to exchange sites was determined by titrating the excess Mg with EDTA (Bascomb, 1964; Environment Agency, 2001).

2.5.3.3. Organic carbon (Loss on ignition – LOI)

Organic carbon content was estimated by measuring the weight loss due to the combustion of organic matter, upon heating at 450°C for 4 hours and

cooling in a dessicator (Sutherland, 1998). Triplicate measurements were made on samples initially dried at 105°C to remove any residual water. Each sample was weighed prior to, and after, heating; the decrease in weight was calculated as a proportion of the initial weight and expressed as a percentage weight loss. The average carbon content of organic matter is approximately 58% (Broadbent, 1953; Rowell, 1994), therefore an estimate of carbon content was calculated by multiplying the measured organic matter content by 0.58.

2.5.3.4. Total metal content: XRFS

Triplicate samples of Stoke Bardolph soil were analysed for total element concentration by wavelength-dispersive X-ray fluorescence spectrometery (Ingham and Vrebos, 1994) and energy-dispersive X-ray fluorescence spectrometry, as described in Rawlins *et al*., (2003); all the analyses and preparations were carried out at the BGS laboratory, operating under UKAS Accreditation. Two Philips PW2400 sequential X-ray fluorescence spectrometers fitted with rhodium-anode X-ray tubes (3 kW 60 kV) were used for Na_2O, MgO, Al_2O_3, SiO_2, P_2O_5, K_2O, CaO, TiO_2, MnO, Fe_2O_3, Sc, V, Cr, Co, Cs, Ba, La, Ce, Nd and Sm as one suite and Ni, Cu, Zn, Ga, Ge, As, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Hf, Ta, W, Tl, Pb, Bi, Th and U as another. A Spectro X-LAB2000 energy-dispersive, polarised, X-ray fluorescence spectrometer fitted with a palladium-anode X-ray tube (400 W 54 kV) was used to determine Ag, Cd, Sn, Sb, Te and I.

Milled material (12 g) was mixed thoroughly with 3 g of binder (EMU120FD styrene co-polymer and one part Ceridust 3620, a micronised polyethylene wax) for 3 min in an agate planetary ball mill before pressing into a 40 mm diameter pellet at 250 kN.

2.5.3.5. Optical methods: XRD and SEM analysis

For bulk and clay fraction XRD analysis, two samples of 20 g of the studied soil (< 2mm) were dried at 55°C for 24 h. Replicate portions were transferred to 4 different 250 ml pyrex beaker and treated with 50 ml of 30% H_2O_2 (hydrogen peroxide) in a water bath (in steps, from 40° to 60°C), in order to remove organic matter. H_2O_2 was added until any reaction had ceased and the suspension left overnight. Samples were then separated into two portions, one for the bulk and one for the clay fraction analysis.

For the bulk fraction, 10 g of material was ground by pestle and mortar; then ca. 3 g were micronised for 3 min, dispersed with de-ionised water, then dried at 55°C, disaggregated (agate mortar) and back-loaded into standard aluminium sample holders for analysis.

The clay fraction was dispersed with de-ionised water for 30 min on a reciprocal shaker and then for 3 min in ultrasonic bath. The sample suspension was passed through a 63µm sieve into a glass cylinder: the retained portion (> 63µm) was washed and dried at 55° C, the filtered portion was decanted into the glass cylinder filled with de-ionised water. Following sample flocculation, 2% *Calgon* solution (sodium hexametaphosphate – $Na(PO_4)_6$) was added until dispersion occurred. The sample was thoroughly shaken and left overnight to let the 63µm equivalent diameter particles settle. For a 20 cm cylinder, nearly 14 hours were required according to Stoke's Law. The first 20 cm from the top (unsettled particles < 2µm) of the cylinder was removed and dried at 55°C. The rest of the suspension was preserved in case more clay extractions were needed. 100 g of the separated dried sample was weighed into a test tube; 3 ml of de-ionised water were added and the suspension placed in an ultrasonic bath to assist dispersion. When completely dispersed, the sample was then applied to a ceramic tile placed on a vacuum cell; when filtration was complete, 2ml of 0.1 M $CaCl_2 \cdot 6H_2O$ solution were added, followed by 2 ml of de-ionised water. The sample was allowed to dry overnight prior to analysis.

XRD analysis was carried out using a Philips PW1700 series diffractometer equipped with a cobalt-target tube and operating at 45kV and 40mA. The bulk samples were scanned from 3-50°2θ at 0.70°2 θ/minute. Diffraction data were initially analysed using Philips X'Pert software coupled to an International Centre for Diffraction Data (ICDD) database.

Following identification of the mineral species present in the samples, quantification was achieved using the Rietveld refinement technique (e.g. Snyder and Bish, 1989) using Siroquant v.2.5 software. This method avoids the need to produce synthetic mixtures and involves the least squares fitting of measured-to-calculated XRD profiles using a crystal structure databank. Errors for the quoted mineral concentrations are typically ±2.5% for concentrations >60 %, ±5% for concentrations between 60 and 30 %, ±10% for concentrations between 30 and 10 %, ±20% for concentrations between 10 and 3 wt% and ±40% for concentrations <3 wt% (Hillier *et al*., 2001). Where a phase was detected but its concentration was indicated to be below 0.5%, it was assigned a value of <0.5%, since the error associated with quantification at such low levels is too large.

Scanning Electron Microscopy (SEM) images and qualitative chemical analysis (EDX) of the soils was undertaken to compare surface morphology and architecture.

Samples were mounted onto SEM sample stubs and painted with silver dag to ensure good electrical contact with the base and sputter coated with a thin layer of gold metal. Samples were examined in a Philips XL30 Scanning Electron Microscope in the secondary electron emission mode using a beam (accelerating) voltage of 15 kV. Qualitative EDX spectra were collected using an Oxford Instruments Link ISIS system, fitted with Si(Li) spectrometer and ultra-thin entrance window allowing detection of light elements down to Boron.

2.5.3.6. Surface speciation analysis: XPS

Theoretical background

XPS technique is concerned with the emission and energy analysis of low energy electrons (generally in the range 20-2000 eV) liberated from the specimen as a result of a particular photoemission process. The excitation source used in this study was AlK_α X-rays (1486.6 eV) with photoemission resulting from the ejection of core level electrons by the AlK_α X-rays. The kinetic energy of the emitted photoelectrons is then analysed by the electron spectrometer and the data presented as a graph of intensity (of counts per second) versus electron energy, the X-ray induced photoelectron spectrum.
The kinetic energy (E_K) of the electron is the experimental quantity measured by the spectrometer, but this is dependent on the energy of the X-ray source employed and is therefore not an intrinsic material property. The binding energy of the electron (E_B) is the parameter which identifies the electron specifically, both in terms of its parent element and atomic energy level. The relationship between the parameters involved in the XPS experiment is as follows:

$$E_B = h\nu - E_k - W \qquad (2.4)$$

where $h\nu$ is the photon energy (1486.6eV for Al K_α X-rays), E_K is the kinetic energy of the electron and W is the spectrometer work function.

As all three quantities on the right-hand side of the equation are known or measurable, it is a simple matter to calculate the binding energy of the electron.

The process of photoemission, where an electron is ejected from the atom, is represented by the photoelectron spectrum: this will reproduce the electronic structure of an element quite accurately as all electrons with a binding energy less than the photon energy will feature in the spectrum.

Those electrons that are excited and escape without energy loss contribute to the characteristic peaks in the spectrum; those which undergo inelastic scattering and suffer energy loss contribute to the background of the spectrum (Fig. 2.8). Since the 'escape depth' is limited to less than 10 nm, only electrons from elements at and near the surface of the solid can be detected and analysed (Paterson and Swaffield, 1994).

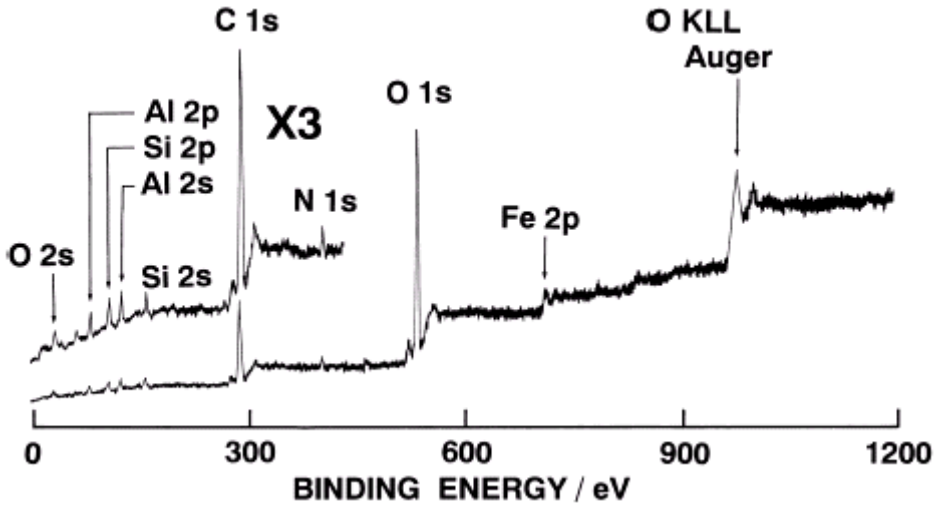


Figure 2.8. Wide-scan X-ray photoelectron spectrum of a soil excited by Al K_α radiation (upper band is the enlargement of the left part of the spectrum – from Yuan *et al.*, 1998).

Once a photoelectron has been emitted, the ionized atom must relax in some way. This can be achieved by the ejection of an electron as an Auger electron.

The nomenclature employed by XPS technique to describe photoelectrons is the so called spectroscopists' or chemists' notation in which electrons are described by the appropriate quantum number and sub-shell, i.e. 1s, $2p_{3/2}$, $3d_{5/2}$, $4f_{7/2}$.

The < 2mm fraction of air-dried soil was gently dry crushed and sieved and used without any further preparation. A small amount of each sample

was spread on to double-sided carbon adhesive tabs, and mounted on 10 mm diameter stainless-steel specimen holders. Sample surfaces were then lightly compacted with an ultra-clean spatula to ensure cohesion of the soil and complete coverage of the carbon adhesive (Gerin *et al*., 1995; Dengis *et al*., 1995).

Samples were analysed on an Escalab Mark I XPS using an unmonochromated Al K_α X-ray source (1486.6 eV) operated at an anode potential of 10 kV and a filament emission current of 20 mA. The vacuum in the analysis chamber was typically better than 4 x 10^{-9} mbar. An electron take-off angle of 90 degrees was used and the area analysed was approximately 1cm x 1cm. The electron spectrometer comprises a hemispherical sector analyser and was operated in the constant energy mode (CAE) at electron pass energies of 10 eV for the high-resolution element peaks. Survey scan spectra were collected in the 0-1100 binding energy range using a pass energy of 50 eV.

Background removal, peak fitting and peak area determination were performed using CasaXPS software. Quantitative data (i.e. atomic % determination) of survey spectra were derived using modified Scofield elemental sensitivity factors. The C_{1s} peak (C-C/C-H) at 285 eV was used to correct the binding energy shift due to charging. This correction was applied to all element peaks following background subtraction/peak deconvolution to give 'true' binding energy values. To ensure correct energy calibration of the spectrometer the calibration was checked before and after the analysis with an argon-etched pure silver standard specimen.

Distribution of carbon in the various chemical states was determined by deconvoluting (i.e. curve fitting) the High Resolution (HR) C_{1s} spectra into components corresponding to known chemical functions (Gerin *et al*., 1995), using a non-linear *Shirley* background model and symmetric peaks with a Gaussian/Lorentzian ratio of 70/30.

Data collection typically comprised a survey analysis followed by an HR analysis of C_{1s}.

The full width at half maximum (FWHM) of the carbon components were typically in the range of 1.4-1.8eV and attributed to carbon in the various oxidation states (see Table 2.6 for details).

2.6. Results and discussion

2.6.1. Soil physical characteristics

Results of the particle size distribution analysis are shown in Fig. 2.9. and 2.10. The Stoke Bardolph soil presented < 9% clay, 40% silt and 45% sand, therefore falling into the category of sandy silt (British Standard classification, see Head, 1992, p. 165). Bulk density (ρ_b) was measured as 0.67 g cm^{-3}, particle density as 1.58 g cm^{-3} (including organic matter); giving a porosity (ε) of 0.58 (void ratio 1.36). These values are more typical of a clayey soil.

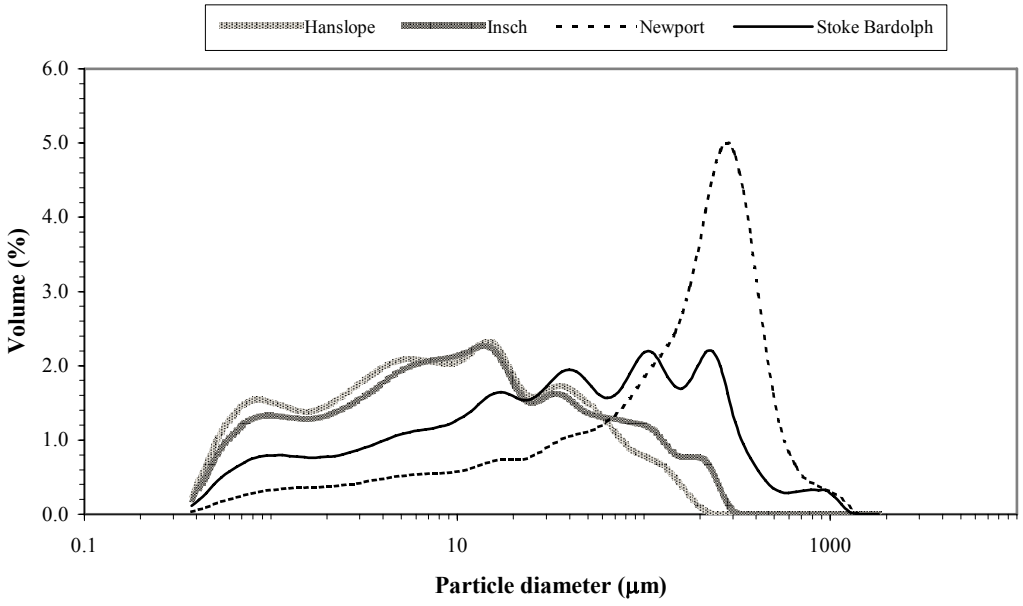


Figure 2.9. Differential volume of particle size as measured by Laser Diffraction Counter for Stoke Bardolph soil compared with three 'test' soils.

It has to be said that the resolution of the laser diffraction instrument is not linear across the entire measuring range, because different size particles scatter light in different ways (Beckman Coulter, 2003). In particular, particles < 1 μm have weaker scattering and are more difficult to discern. For these reasons a different technology (i.e. Polarisation Intensity Differential Scattering - PIDS) is generally used for the high resolution of sub-micron particles[3], but was not employed in this context. Therefore, results may be slightly underestimating the clay content and differ from the published data for the soils presented here (e.g., Memoirs of Soil Survey, various sheets). Nevertheless, the Fraunhofer approximation used for the measurements gives good results over the range considered (ISO, 1999).

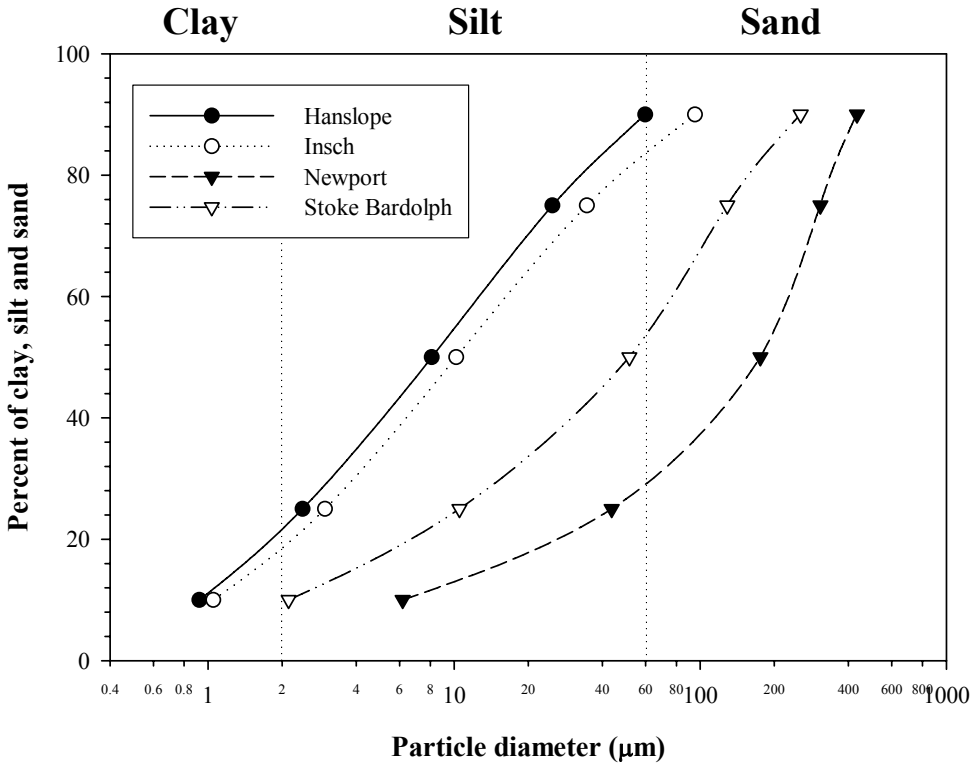


Figure 2.10. Particle size distribution curves for Stoke Bardolph soil compared to three 'test' soils (Hanslope, Insch and Newport).

[3] See http://www.beckman.com/products/instrument/partChar/technology/pids.asp for more information on the technique

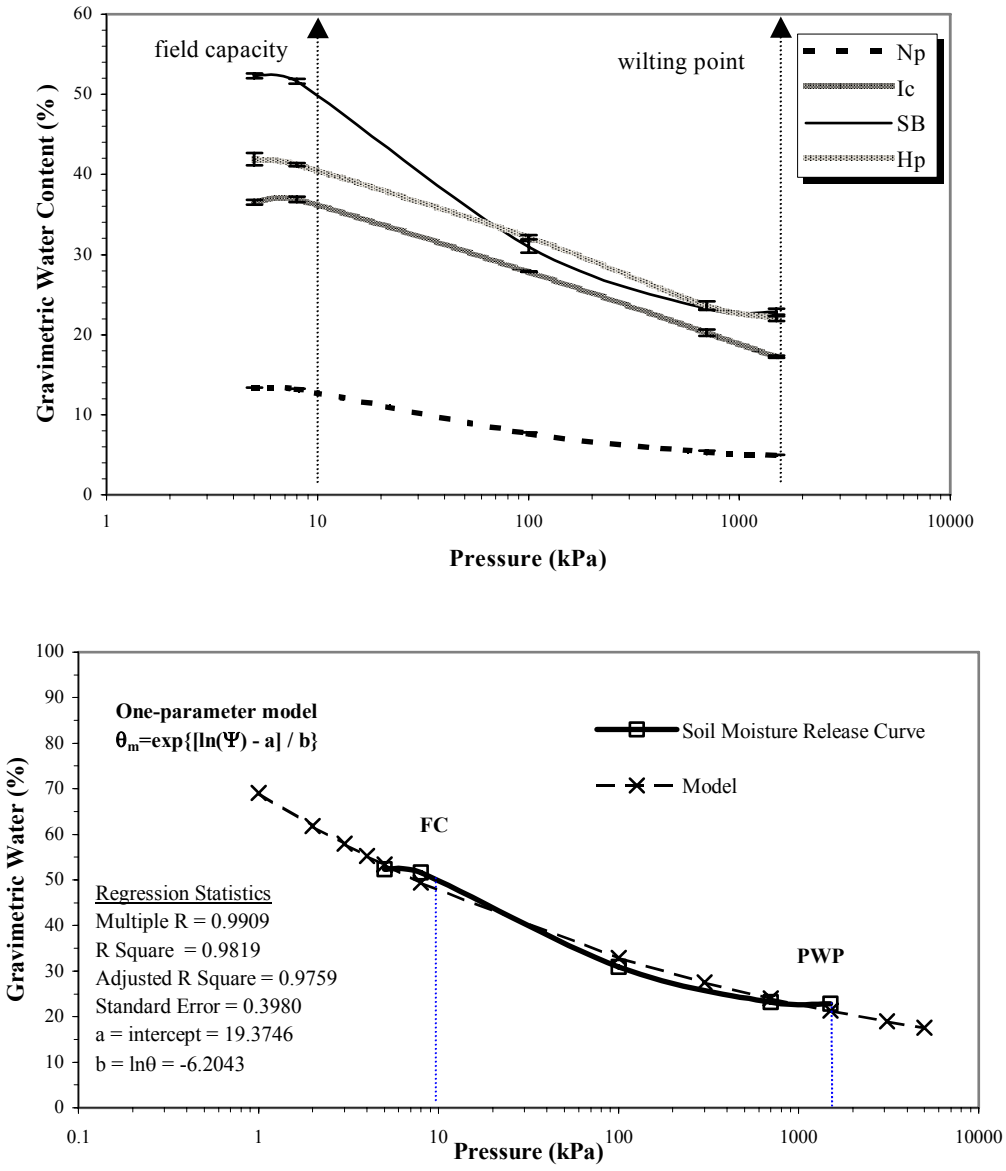


Figure 2.11. a) Water characteristic curves for Newport (Np); Insch (Ic); Stoke Bardolph (SB); and Hanslope (Hp) soils; b) comparison of experimental and modelled (one-parameter model – Gregson *et al.*, 1987) water characteristics curves for Stoke Bardolph soil; vertical bars represent standard errors.

Water characteristic curves for the Stoke Bardolph soil is given in Fig. 2.11a and b, where it is also compared with the other three 'test' soils. The curves reflect the textures of the soils; SB is behaving very similarly to a clayey soil with a steeper slope of the curve at between low and medium

suctions. Conversely, the three 'test' soils present fairly typical shapes with respect to their textures. The different behaviour by SB is clearly due to the amount of organic matter in the soil. Organic matter produces both a direct and indirect effect on the amount of water held in a soil (Brady and Weil, 1999).

Organic matter is generally more porous than mineral soil particles and can hold much greater quantities of water than that of an equal volume of mineral matter when the soil is between FC and wilting point (Hudson, 1994). The indirect effect of organic matter occurs through its influence on soil structure and total pore space. Its presence helps to stabilize soil structure and increases the total volume as well as the size of the pores. This therefore organizes the aggregate structure of the mineral phases so as to increase the occurrence of 'storage pores'.

Table 2.5. Total available and capillary water of the four test soils.

Soil	FC (-10 kPa)	PWP (-1500 kPa)	Hycroscopic coefficient* (-3100 kPa)	Capillary water†	Available Water θ_m (g g^{-1})
Newport	0.1331	0.0493	0.0413	0.0918	0.0838
Insch	0.3652	0.1726	0.1632	0.2020	0.1926
Hanslope	0.4191	0.2203	0.2029	0.2162	0.1988
Stoke Bardolph	**0.5231**	**0.2286**	**0.1892**	**0.3339**	**0.2945**

*estimated using Gregson *et al*. (1987) model
†difference between FC water and Hygroscopic water

The "one-parameter model" proposed by Gregson *et al*., (1987) was fitted to the experimental data (Fig. 2.11b). The model shows a very close fit to the data, where similar results are achieved with the 'test' soils (data not shown). The model was used for calculations of water retention (Fig.2.12). Table 2.5 shows values of field capacity FC (- 10 kPa), wilting point PWP (- 1500 kPa) and available water content θ_m for the soils studied, as well as estimates of capillary water and water content at the hygroscopic coefficient.

The Stoke Bardolph soil showed a greater capacity to hold capillary water compared to the other soils, even compared to the clayey soil.

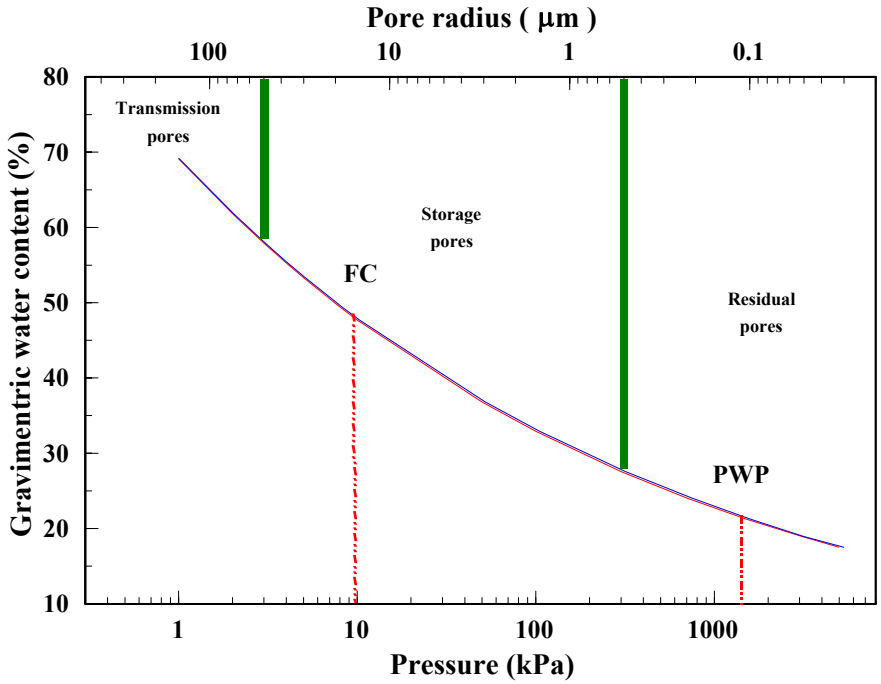


Figure 2.12. Modelled moisture characteristic of Stoke Bardolph soil with equivalent pore size distribution and pore classification (Greenland and Hayes, 1981).

2.6.2. Soil chemical characteristics

Table 2.6 shows the result of the XRF analyses and lists the mineralogy and some of the chemical parameters measured. As expected, all of the trace elements were enriched and their concentrations exceeded those found in average uncontaminated soil (see Table 1.1). The most abundant trace elements were Zn, Cr, Cu, followed closely by Pb and Ni. It is also interesting to note the values for Sn (170 mg kg^{-1}), Sb (75 mg kg^{-1}), V (57 mg kg^{-1}), Cd (50 mg kg^{-1}), and As (34 mg kg^{-1}), which are all well above typical concentrations in soils (see Table 1.1). Given the coarse texture of the soil and its low clay content, CEC will be provided mainly by humus content. Considering the clay and SOM contents, their relation and the consequent influence on CEC

will roughly be 1:3. Therefore, while 46.7 $cmol_c\ kg^{-1}$ can be ascribed as SOM-derived exchange sites, only 15.6 $cmol_c\ kg^{-1}$ are probably due to the clay fraction.

X-ray diffraction profiles of the soil studied are shown in Fig 2.13, 2.14 and 2.15, with the main phases observed listed in Table 2.6. The XRD data illustrate the presence of mostly commonly occurring soil minerals, with quartz, calcite and dolomite identified as the major mineral phases from the XRD data of whole-rock sample (bulk sample), and minor amounts of Feldspar (possibly microcline), albite, kaolinite, muscovite. A peak possibly associated with a hydrated zinc phosphate hydroxide (possibly *spencerite*) was also identified. Zinc is the most abundant of the heavy metals and phosphates are highly enriched on the sampling site (141-200 mg P kg^{-1} bicarbonate-extractable P, Young *et al*., 2000).

Table 2.6. Major and trace element concentrations in SB soil as measured by XRF, mineralogy and some chemical parameters; all values in mg kg^{-1} unless otherwise stated.

Element	Concentration	Element	Concentration	Mineralogy		Soil chemical parameters	
CaO (%)	9.06	**As**	34.5				
Fe_2O_3 (%)	3.83	**Br**	32.5	Quartz	SiO_2		
K_2O (%)	1.05	**Ag**	30.0	Calcite	$CaCO_3$	**pH**	6.32
TiO_2 (%)	0.392	**Nd**	27.5	Dolomite	$(Ca,Mg)CO_3$		
MnO (%)	0.142	**La**	24.0	Feldspar	$(Na,K)AlO_2[SiO_2]_3$	**CEC**	62.3 $cmol_c\ kg^{-1}$
		Co	20.5	Albite	$NaAlSi_3O_8$		
Zn	2946	**Y**	18.0			**LOI**	27.1 %
Cr	2604	**W**	12.5	Kaolinite	$Si_4Al_4O_{10}(OH)_8$		
Ba	2099	**Sc**	11.0	Muscovite	$KAl_2(Si_3Al)O_{10}(OH,F)_2$	**Organic C**	15.7 %
Cu	1194	**Ga**	8.00	Zn phosphate	$Zn_4\ (PO_4)_2\ (OH)_2\ \cdot 3H_2O$		
Pb	850	**Nb**	7.50	Illite	$(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$		
Ni	571	**I**	7.50				
Sn	170	**Ge**	6.50	Ca oxalate hydrate	$CaC_2O_4\ \cdot 2.25\ H_2O$		
Sr	160	**Hf**	5.00	Fe, Mn phosphate	$(Fe, Mn)_3\ (PO_4)_2\ (OH)_2$		
Zr	140	**Th**	4.50				
Sb	75.0	**Mo**	4.00				
Bi	60.5	**Se**	3.00				
V	57.0	**Sm**	2.50				
Cd	50.5	**Ta**	2.50				
Ce	47.5	**U**	2.00				
Rb	44.5	**Tl**	<1				

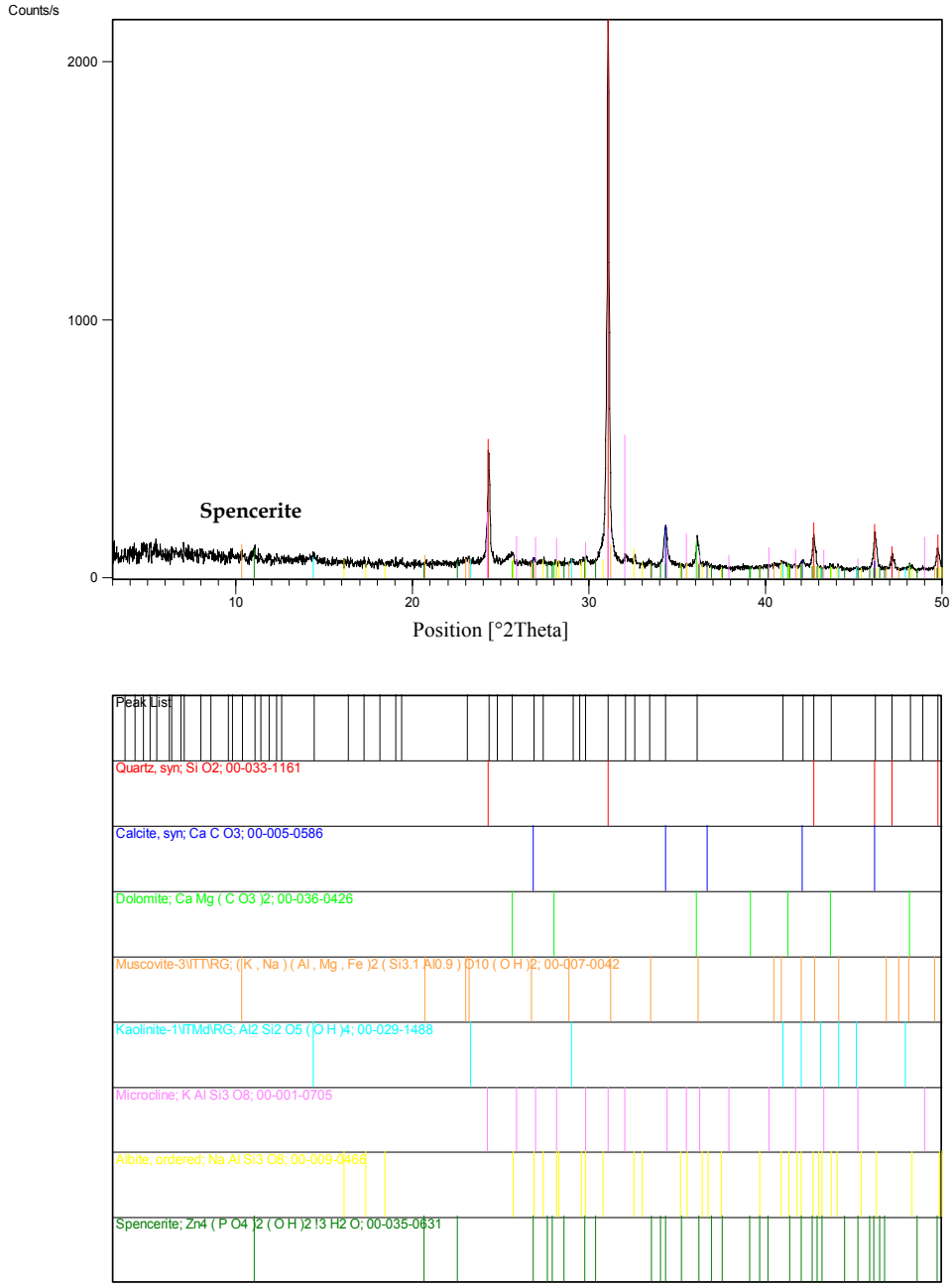


Figure 2.13. X-ray diffractograms of Stoke Bardolph soil for the bulk fraction.

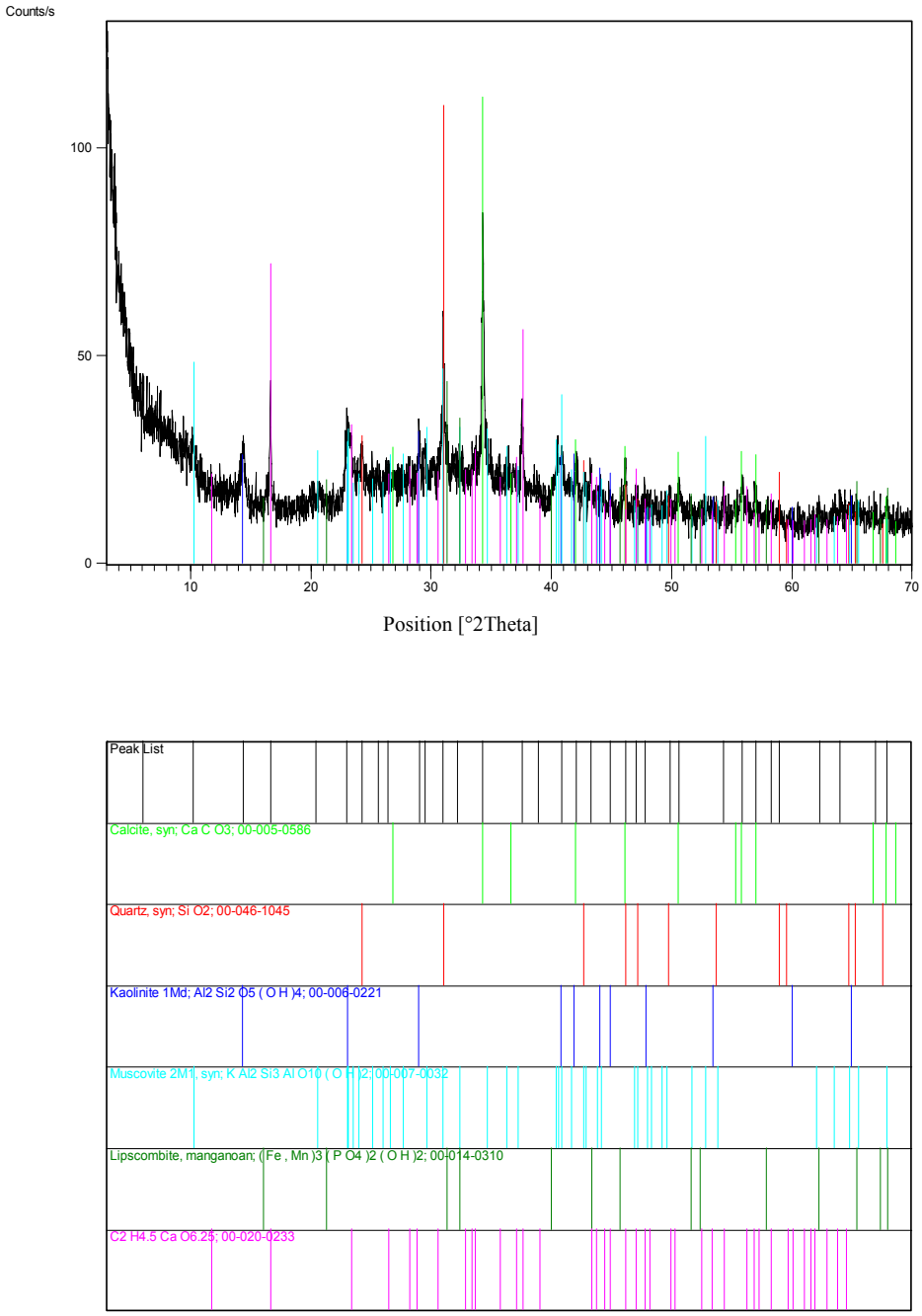


Figure 2.14. X-ray diffractograms of Stoke Bardolph soil for the < 2µm fraction.

The diffractogram for randomly oriented < 2 µm size fraction shows similar results, with quartz, calcite, kaolinite and muscovite present. Illite

and two new phases appear in the oriented mount; a hydrated calcium oxalate (possibly *weddelite*) and an iron manganese phosphate hydroxide (possibly *lipscombite*).

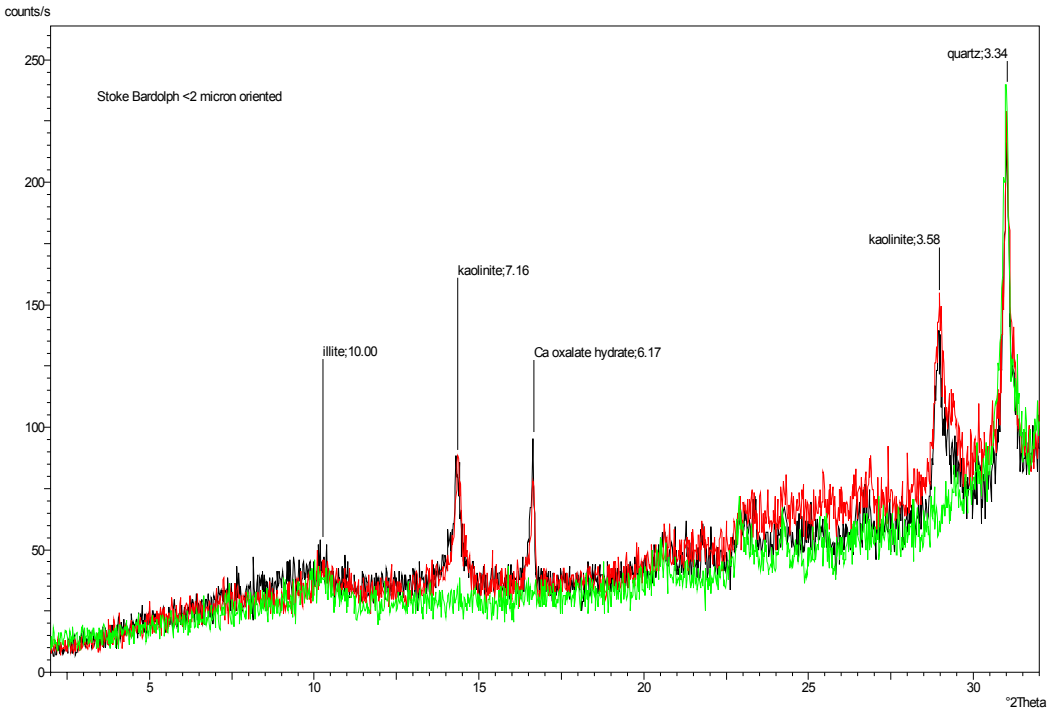


Figure 2.15. X-ray diffractogram of the < 2 µm size fraction with oriented mount for Stoke Bardolph soil; d-values in in Å are noted alongside the mineral names.

Calcium oxalate could well be a by-product of the H_2O_2 treatment to separate the organic matter, whereas the phosphate could be a result of the sewage sludge amendment, similarly to the zinc phosphate observed in the bulk sample. The majority of the phosphate is however likely to be present as Ca-phosphate, probably in the forms of hydroxylapatite [$Ca_5(PO_4)_3OH$], tricalcium phosphate [$Ca_3(PO_4)_2$], or octacalcium phosphate [$Ca_4H(PO_4)_3{\cdot}2.5H_2O$]. Ca-phosphates should have a characteristic peak corresponding to 2.81 Å which is not showing on the XRD diffractograms probably because of interference from organic carbon phosphate or humic acid. However, the crystalline phases could be superseded by a widespread unstable amorphous phase.

The presence of base metal phosphates is sometimes explained by the presence of ferromanganese oxyhydroxides, which promote the interaction of the base metals with P by serving as an adsorbent and a retaining matrix for both P and the base metals (Nriagu, 1984). When the particles settle out, base metals are immediately exposed to pore water with elevated concentrations of orthophosphate ions (Nriagu and Dell, 1974), and the interaction of the metals with the orthophosphate ions may be expected to occur.

The occurrence of quartz, kaolinite, calcite and feldspar in the < 2 µm fraction could suggest association with other lower density materials, such as organic matter or amorphous material, highlighting the difficulty in disrupting the physical organic-inorganic interaction in sewage sludges-amended soils (Essington and Mattigod, 1991). The noisy background observed in the diffractograms indicates that amorphous material is present in the sample, and makes interpretation difficult. The history of the site, as a lagoon for sludge de-watering, the high phosphate inputs and the rigorous liming protocol followed, may support the evidences of amorphous material. In a previous study of the same Stoke Bardolph soil, SOM showed profiles enhanced down to ca. 60 cm depth, suggesting strong interference with the mineral phase throughout (Maxted, 2003, data not shown).

The latter observation was also supported by the SEM-EDX images, which showed a high amount of amorphous material, either isolated or coating the particle surfaces, whereas the crystalline phases were often identifiable as quartz and/or calcite (Fig 2.16). Particles coatings could be either organic material (humic and fulvic acids) and/or Fe, Mn oxyhydroxides, but the EDX spectra cannot resolve this aspect.

Fig. 2.17 shows the wide-scan XPS spectrum covering a binding energy (E_B) from 0 to 1250 eV. This is clearly dominated by peaks for O, C and Si, with less Al, Ca and N. Elements including Fe, Cr, Ni, S, P and K, which were

detected by SEM-EDX, were not detected here, probably because they were below detection limits or absent from the surfaces. The absolute intensities of photoelectron peaks are influenced by factors such as density, chemical composition and surface roughness of the sample (Vempati *et al.*, 1996).

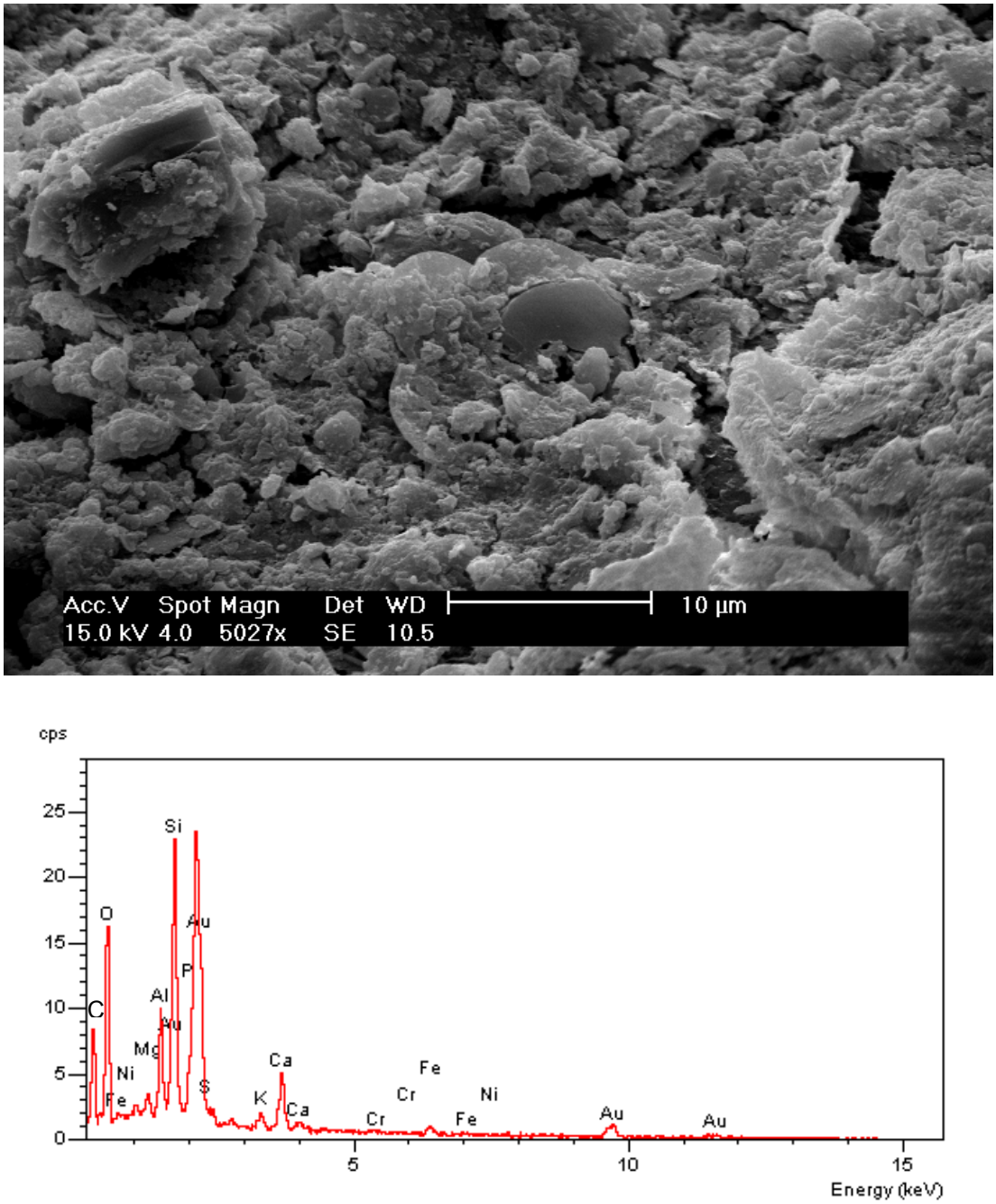


Figure 2.16. Secondary electron micrograph image and EDX spectrum of elemental chemical composition of Stoke Bardolph soil (Au coated).

Concentrations of C and N observed in the spectra are ascribed to OM in the soil. Nitrogen was detected at a binding energy of 399-400 eV, corresponding to N in organic amine or amide (Gerin *et al.*, 1995). This represents strong evidence that the OM in the samples occurs as a coating over particle surfaces as well as being dispersed throughout the whole samples.

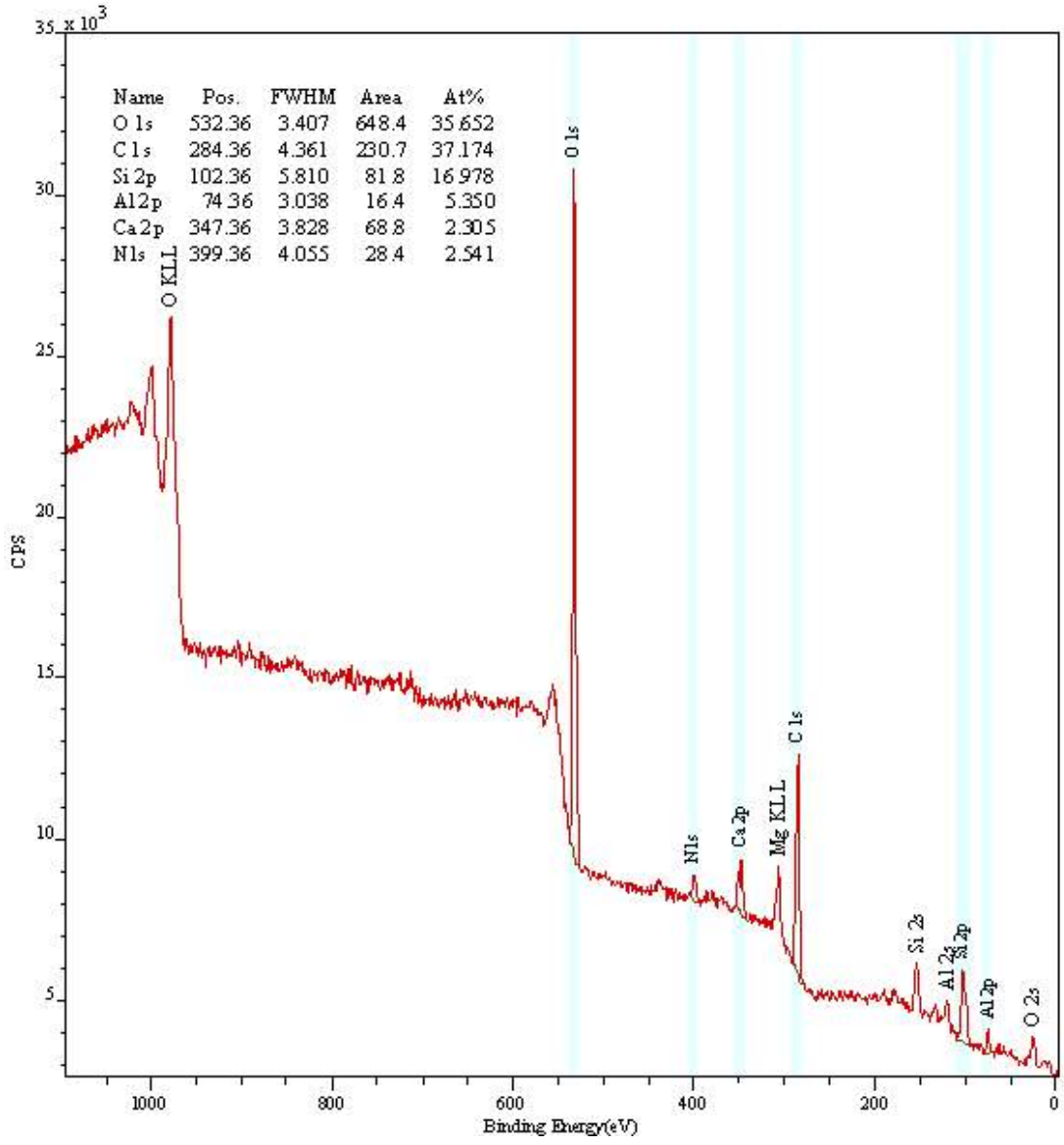


Figure 2.17. Wide-scan X-ray photoelectron spectrum (0-1250 eV) of Stoke Bardolph soil excited by Al K_α radiation.

The Hanslope, Insch and Newport soils showed similar results to that for SB soil, in agreement with recent studies (Yuan *et al*., 1998; Gerin *et al*., 2003), strongly indicating that OM occurrence as a coating over particle surfaces is probably most likely even at much lower total organic contents. The presence of Al on surfaces, could arise from an association with OM (Courchesne *et al*., 1996), other Al silicates or Al in kaolinite. The Ca peak is probably related to the very high content of CaO subsequent to the liming regime on the SB site.

For each visible peak, a narrow-scan spectrum (10 eV) was also determined: this can help discriminate the chemical composition at the surface. In particular, carbon was analysed in order to interpret its distribution in the various oxidation states (Fig. 2.18 and Table 2.6). Results indicate that $C^{[0]}$ and $C^{[+1]}$ (where the exponent in square brackets indicates valence states), are the main components, with 47.5 and 38.1% respectively, with a lesser amount of carboxylic acid and/or carbonate ($C^{[+2]}$ or $C^{[+3]}$ depending on protonation). These results are in agreement with the recent work by Gerin *et al*., (2003). These authors also compared the mean functional C composition as determined by XPS with the composition of purified humic and fulvic acids as determined by wet chemistry (Schnitzer, 1978) and ^{13}C-NMR (Cook and Langford, 1998). They found that there was good agreement between the composition of organic substances determined by XPS with the bulk composition of humic acids. Therefore, it may be reasonable to think that these are the conditions that are most likely to exist for the soil studied as well, with humic acid present in larger proportions compared to fulvic acids.

Table 2.7. Types of functional groups that were considered in the de-convolution of the carbon spectra (from Gerin *et al*., 2003, according to Gerin *et al*., 1995)

Type of Carbon	Fitting notation	Valence notation	Binding energy eV
C-C, C-H	a	$C^{[0]}$	284.8
C-O, C-N	b	$C^{[+1]}$	286.4
C=O, O-C-O	c	$C^{[+2]}$	287.9
O=C-O, O=C-N, CO_3^{2-}	d	$C^{[+3]}$	289.3

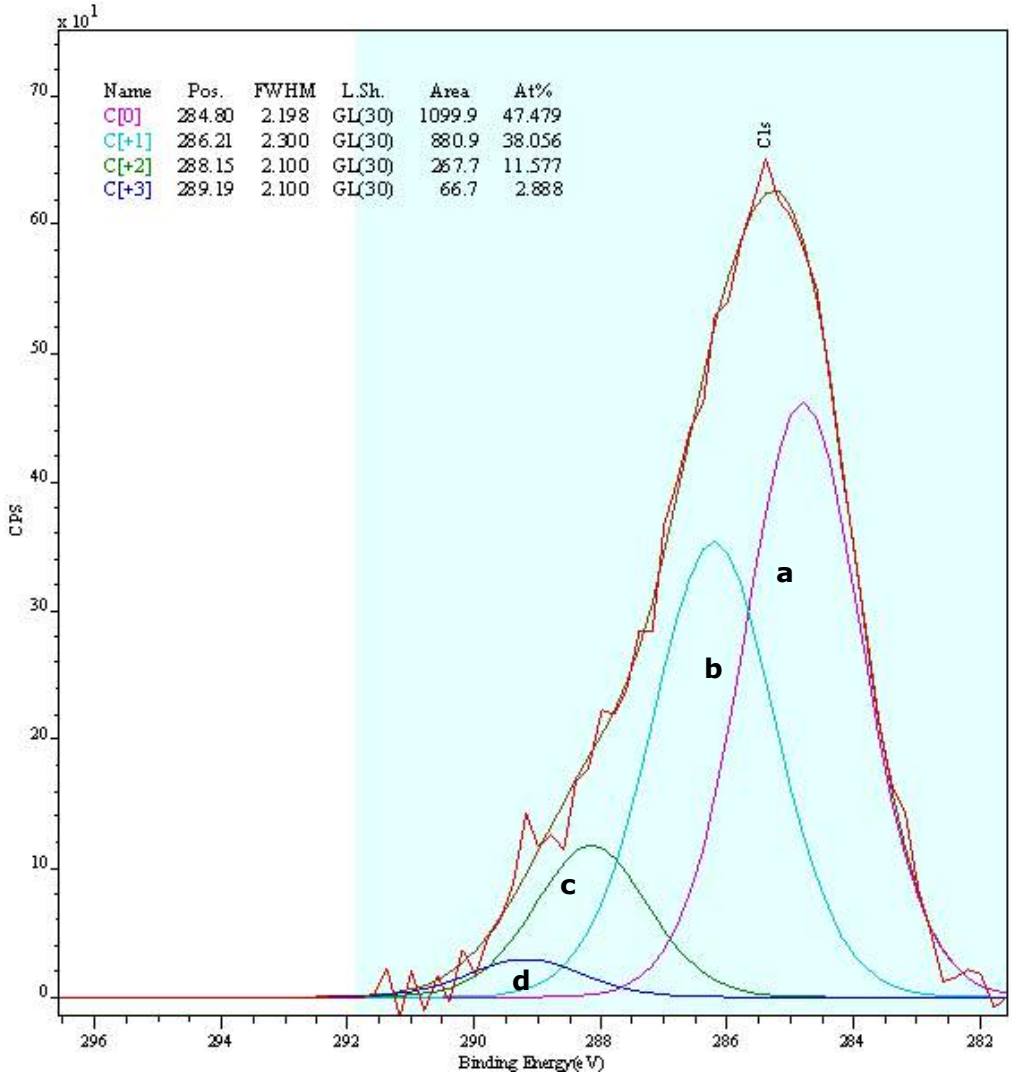


Figure 2.18. Observed C(1s) spectrum 'e' of Stoke Bardolph, with computer fit components 'a 'b 'c' and 'd', indicating different C oxidation states (see also Table 2.6.)

2.7. Conclusions

Te principal soil studied (Stoke Bardolph) was characterised for its major chemical and physical properties. As anticipated the soil showed high concentrations of trace elements as a result of historical additions of sewage sludge (Table 2.6). Mineralogical analysis illustrated close matching with the

mineralogy of the soil parent material. Solid phases were also identified which probably originate from amendment with sewage sludge.

The soil has high humus content which, in turn, influences other properties, including CEC, phosphate content, bulk density, and FC. The soil is classified as a sandy silt (Particle Size Analysis - PSA), with < 9% clay. Its CEC was however relatively high, with roughly 75% of total exchange sites ascribable to SOM. This will affect the capacity of the soil to retain and exchange metals with the liquid phase, especially as OM is coating the surfaces of the mineral particles. The nature of the carbon coating particle surfaces is dominated by material of humic rather than fulvic composition.

Bulk, particle density and total porosity (in terms of 'storage pores') was also affected by the presence of SOM. Water retention is enhanced by the OM, as is FC. This finding is supported by the high volume of capillary water available in the soil (storage and residual pores), which far exceeded that of the other three soils tested.

3. Soil pore water extraction methods

3.1. Introduction

There are several approaches to sampling soil pore water from soils, however no single methodology is appropriate to all applications. The choice of method will depend on the particular aim of the study in question. In fact, it is arguable that soil pore water is operationally defined by the methodology employed for its acquisition and subsequent analysis. It is therefore very important to describe the methodology and the assumptions employed.

This chapter describes some current methodologies used to extract soil pore water. Three laboratory-based methods (Rhizon™ samplers, centrifugation, and pressure filtering) were chosen for further investigation and considered in detail. Results are presented for a range of operational factors: pressure applicable (i.e., pore size involved), moisture pre-requisites of the soil, pore water yielding, efficiency, duration of extraction, materials and possible contaminations for trace metals studies.

3.3. Pore water extraction methods

3.3.1. Field-based methods

Field methods for sampling pore water are generally grouped under the general term ***lysimetry***. This definition usually comprises a range of types of samplers (Wolt, 1994):

- Monolith – any device using an undisturbed soil block or column;
- Filled-in – devices containing soil where the natural soil structure has been disrupted;
- Tension – also called vacuum, suction, point or mini - lysimeters;
- Passive – also called capillary samplers, zero-tension – lysimeters;

- Ebermayer – any lysimeter installation where, by access from a trench, a trough, pan, funnel, plate, or wick is placed under undisturbed soil.

Of these, tension and passive samplers are the most widely used and are discussed below.

3.3.1.1. Tension samplers

In general, the approach employed for extracting pore water *in situ* is to use tension samplers such as porous cups, (for a complete review see Litaor, 1988; Grossmann and Udluft, 1991). Porous cups are designed to replicate the function of a plant root, by applying suction to the soil. The method however is replete with inadequacies that need to be considered in the acquisition and interpretation of data. Principal limitations are the non-representative sampling of soil water occurring above the capillary fringe, and potential artefact effects arising from the reaction of lysimeter materials with the surrounding soil environment. In the first instance, changing the applied vacuum (from 0 to – 40 kPa) was observed to generate little effects on the concentrations of chemical species collected (Beier and Hansen, 1992; Beier *et al*., 1992). Additionally to this, water will flow from the soil into the porous cup if the capillary pressure in the cup is lower than that in the soil. With a single pump, a vacuum of – 90 kPa can be easily generated and applied to the samplers. Sampling seepage (i.e. slowly percolating) water is therefore possible only as long as the capillary pressure in the soil lies above this value. As a result of the low sampling rates at capillary pressures below – 70 kPa, the use of this system is limited in the majority of soils (Grossmann and Udluft, 1991).

The other problem connected with the use of these samplers is the sorption of solutes from the pore water. Depending on the cup material (materials used include aluminium oxide, glass sinter, ceramic, teflon, acrylic copolymer with internal nylon support, stainless steel, plastic 'organic'

polymers – PVC, PP, PVDF) additional reactions may take place leading to absorption, precipitation or even release of chemical substances, resulting in pronounced effects on the final composition of the water sampled (Litaor, 1988). Several studies have investigated these effects and questioned the validity of results given by these kinds of samplers (e.g., Hansen and Harris, 1975; Levin and Jackson, 1977; Nagpal, 1982; Guggenberg and Zech, 1992; Goyne *et al*., 2000). Siemens and Kaupenjohann (2003) found that between 0.8 and 63 mg L^{-1} of dissolved organic carbon (DOC) was released from sealing and glues of pore water samplers. They concluded that samplers should be designed without glues or elastomers, presenting a suction plate entirely made from borosilicate glass that did not release organic C. Interaction with organics may be particularly significant in the case of trace metals adsorption on the surface of the samplers (Shendrikar *et al*., 1975; Massee and Maessen, 1981; Grossmann *et al*., 1990; Wenzel and Wieshammer, 1995; Wenzel *et al*., 1997). Different materials have been tested to minimize metals sorption effects. For example, McGuire *el al*., (1992) found that metal adsorption on samplers decreased on porous cups made of materials in the sequence ceramic > stainless steel > fritted glass = poly(tetrafluorethene) (PTFE), with trace metals being adsorbed in the sequence Zn >> Co > Cr > Cd. These authors also pointed out the importance of the total metal concentration as well as cleaning method (water vs acid solution) and rinse volumes, which affected the extent of the adsorption. Adsorption was between 2 to 15 times higher for water-cleaned samplers, but also increased on acid-cleaned samplers with decreasing volumes utilised. A later study by Andersen *et al*., (2002) found that cups made of PTFE affected the concentrations of Cd, Cu, Ni and Zn, which were adsorbed at pH > 4.5 for low pore water concentrations. Results on adsorption showed that plastic cups may have some advantage over conventional ceramic cups. With increasing sample volume the concentration of a trace metal recorded by the suction cup comes closer to the concentration in the pore water because of the equilibration of

the cation exchange surface of the suction cup with the solution. However, the extraction of large sample volumes can cause a significant disturbance of the system (Grossmann and Udluft, 1991). More recently, ceramic cups were found to adsorb PO_4^{3-}, DOC, major and minor cations (Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe^{3+}, Al^{3+}, Mn^{2+}, and Zn^{2+}) and SO_4^{2-} and NO_3^- anions. They release H_4SiO_4 and, in addition to this, relative low pH values (5.1 – 6.2) favoured anion and DOC adsorption, the latter increasing the exchange capacity and cation adsorption of the material (Menendez *et al*., 2003).

Despite the potential problems, this remains an area of great opportunity for innovation, as illustrated by the development of new types of sampler, such as the soil moisture Rhizon samplers (www.eijkelkamp.nl), which will be described later.

3.3.1.2. Passive samplers

Passive samplers have no tension applied to them. Consequently, they only sample that fraction of the soil water flux occurring under saturated soil conditions or during macropore flow. These devices results in samples of soil water which may represent a combination of bypass water (recent rainfall, irrigation events, i.e. water moving *via* preferential flow), and "internal catchment water" (Booltink and Bouma, 1991), i.e. water moving by diffusion and/or conduction and exhibiting a range of contact times with the soil matrix. The proportion of bypass water compared to internal cachment water will depend on soil structure, soil moisture conditions prior to and during percolate sampling, and features of the design and operation of the lysimeter. As a result, compositional analysis of 'passive' lysimeter solutions and pore water obtained by laboratory displacement may substantially differ (Zabowsky and Ugolini, 1990).

3.3.2. Laboratory-based methods

Laboratory methods of pore water displacement are designed to approximate diffuse water in quasi-equilibrium with the soil solid phase. Methodologies for obtaining "unaltered" soil pore water in a laboratory setting may be broadly defined as ***displacement techniques*** and comprise:

- Column displacement (pressure or tension displacement, with or without a displacing head solution);
- Centrifugation (with or without immiscible liquid displacement);
- Saturation extracts (including saturation pastes);
- Water extracts;
- Complexation and exchange techniques (e.g., DGT technique, Hooda *et al*., 1999);
- Lysimetric methods (both tension and passive, including Rhizon samplers - see also field methods)

The various column displacement methods are the most widely applicable and reliable techniques, although require a high degree of operator experience. Centrifugation methods are the most popular soil pore water displacement techniques due to their ease and the ready availability of the requisite equipment in most laboratories. Saturation extracts constitute a valid alternative, especially when batch experiments are carried out (Degryse *et al*., 2003).

3.3. Choice of methods

From the preceding discussion (see also sections 1.3. and 2.3.) it is apparent that the sampling procedures used for this study should be capable of identifying the origin of pore water sampled. In general, most field sampling methods have been used to interpret soil pore water chemistry from both static and dynamic perspectives, without sufficient consideration of which soil water is being sampled and its chemical reactivity in soils (Wolt, 1994). This possibly makes field-based sampling more suitable than

laboratory methods for consideration of chemical transport, provided the solutions obtained represent mobile water in the soil environment. By contrast, considerations of biologically important processes relating to plant nutrient availability, phytotoxicity and soil metabolism are probably best related to chemical composition of diffuse soil water as reflected in the composition of displaced soil pore water. Therefore, it may be reasoned that laboratory methods appear more appropriate for this project.

Three different extraction methods were chosen for this project:

1) Rhizon samplers (or 'Soil Moisture Samplers' - SMS);
2) drainage centrifugation;
3) 'pressure filtering' (squeezing).

These three methods were selected for different reasons, but mainly for their flexibility and novelty. Rhizon samplers represent the current equivalent of porous cups, widely used in the recent past, centrifugation is possibly the current most widely used method and squeezing is a novel alternative, since it has been never used on soils before and has the potential to access water contained in small pores. These methods should enable us to perform 'fractionated' extraction on the soil, whereby a combination of the methods can be used to provide soil water originating from a wider range of pores.

3.3.1. Rhizon Soil Moisture Samplers (SMS)

Rhizon samplers are a hybrid device, which can be used in the laboratory for e.g. pot experiments, as well as in the field (Knight *et al*., 1998; Cabrera, 1998). They represent one of the latest developments in terms of tension samplers, where it is necessary to apply a suction to withdraw pore water, either with a syringe, a vacuum tube or a pump. In this project Rhizon samplers obtained from Rhizosphere Research Products (Wageningen, Holland), and later from Eijkelkamp (www.eijkeljamp.nl), were used.

A pore water sample is obtained by inserting the sampler into a wet soil, and applying a suction from a vacuum tube or syringe. According to the manufacturer, the yield in water with 100 kPa pressure differential is greater than 1 ml min^{-1}.

Rhizon samplers are becoming increasingly popular, especially for studies on bioavailability. Knight *et al*., (1998) were one of the first group of researchers to apply these devices to extract pore water for metal availability studies (Cd, Zn) on soil pore water. Applications on nutrient properties and distribution in different media are also found (e.g. Cabrera, 1998). The methodology has been compared with centrifugation for microbial ecotoxicity testing on soil amended with Cd and Zn (Tiensing *et al*., 2001). Luo *et al*., (2001, 2003) studied Cu and Zn in polluted soil as influenced by γ-radiations, monitoring the changes in metal concentration over time. More recently, the same authors evaluated the use of a multi-layer column device, with installation of Rhizon samplers, to collect soil pore water for study on nitrate leachability in sludge-amended soils. Rhizon samplers were also used by Tye *et al*., (2002, 2003) to extract pore water to predict As solubility in contaminated soils and to study Cd^{2+} and Zn^{2+} activities in soil pore water on a range of soils.

3.3.2. Centrifugation

Centrifugal extraction of pore water is a relatively routine and well-established method. Its use started early in the 20th century (Cameron, 1911), but was little used until its reintroduction by Davies and Davies (1963). Since then few modifications have been applied to the method. Generally, one can distinguish between three main kinds of centrifugation: low-pressure centrifugal displacement or high-pressure centrifugal displacement and centrifugation with immiscible liquid (Fig. 3.1).

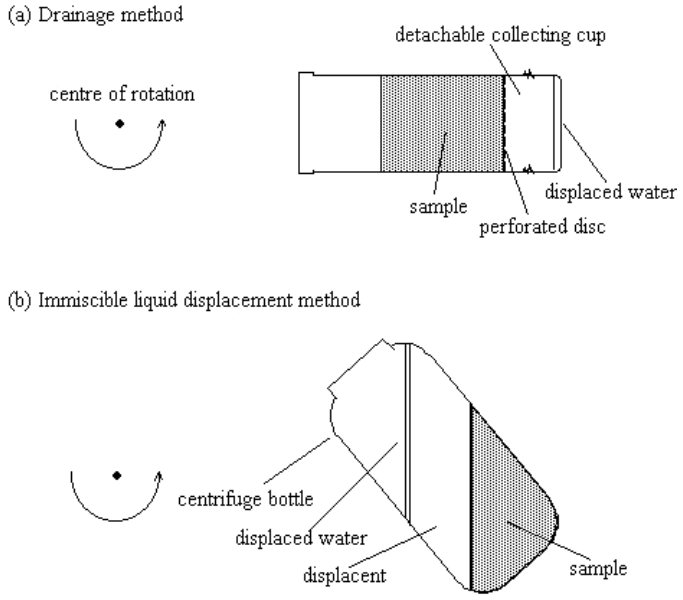


Figure 3.1. Pore water extraction by (a) drainage centrifugation using a swing-out rotor and (b) immiscible liquid displacement using a fixed-angle rotor (after Kinniburgh and Miles, 1983).

The first two types are based on free drainage of the pore water, through a porous plate supporting the sample, into a collecting cup. The third is based on the displacement of pore water by a dense, immiscible liquid followed by subsequent collection of the displaced water after it has floated to the top (Mubarak and Olsen, 1976; Batley and Giles, 1979; Whelan and Barrow, 1980; Kinniburgh and Miles, 1983).

Centrifugation has been widely applied to the extraction of pore waters from various materials including sediments, chalks, sandstones and clayey soils (e.g. Shaffer *et al*., 1937; Richards and Weaver, 1944). Drainage centrifugation was reported as a method for the removal of fluids from various saturated and partially saturated geological materials in the early soil science literature. These early studies were aimed at measurements of the physical properties of the rocks rather than the characterisation of extracted pore waters. Jones *et al*., (1969) and Sholkovitz (1973) later reported the use of centrifugation, to extract pore water from basin sediments for chemical characterisation. Much of the sampling of pore water in hydrochemical

investigations in UK aquifers follows the approach developed and tested in the pioneering work of Edmunds and Bath (1976). The same high-speed centrifugation technique adopted by these authors was later used by Wheatstone and Gelsthorpe (1982) and others for the extraction of pore waters from Triassic sandstones. The technique gradually became the preferred method in soil science. Adams *et al.*, (1980) reported that centrifugal displacement at low pressures (< 500 kPa) represented the most widely employed approach to obtaining soil pore water.

The direct centrifugation drainage technique is often preferred as a simple way of obtaining pore water that minimises risks of contamination (Tyler, 2000). Centrifugation allows the quick and easy removal of soil water at precise intervals in time at matric suctions greater than 100 kPa, the upper limit of most of the porous ceramic samplers (Jones and Edwards, 1993). The pressure applied can go up to 1500 kPa with the highest centrifugal speeds.

Many researchers have tested and reported the yield (defined also as "extraction efficiency" – Entwisle and Reeder, 1993, see methods in this chapter) for different materials and using a range of rotation speeds and lengths of operation. In the study of Edmunds and Bath (1976), extraction yields of 20-30% were obtained at low speeds, compared with up to 85-95% of the available pore water using the high-speed centrifuge. In the study of Wheatstone and Gelsthorpe (1982), the moisture content of the samples tested varied between 6 and 15% and the percentage of water extracted increased with increasing speed from 3000 to 12000 rotations per minute (rpm). At the optimum speed of 12000 rpm, tests showed that only a marginal increase in the amount of fluid extracted was observed after an initial 30 minutes operation. In the work of Kinniburgh and Miles (1983), yields were typically 20 to 50% for soils of moisture content 10 to 40%, but up to 90% for some chalks with 20% initial moisture content.

Studies comparing different centrifugation methods and other techniques in providing soil pore water have been reported by many authors (e.g. Menzies and Bell, 1988; Zabowski and Ugolini, 1990; Sheppard *et al*., 1992; Dahlgren, 1993; Lorenz *et al*., 1994; Giesler *et al*., 1996; Chapman *et al*., 1997a). Most studies are fairly consistent in their illustration of the differences among methods in terms of element concentrations in pore water, partly due to different fractions of pore waters considered. Moreover, centrifugation can be used to fractionate the pore water by selecting several centrifugation rates, i.e. pore water can be extracted using a number of steps, with an increment of centrifugal speed. When increasing the centrifugal speed, and therefore the relative centrifugal force (RCF) value, during the various stages of soil centrifugation, less available water may gradually be released and collected (Tyler, 2000), thereby extracting water from a range of pore size distributions. Centrifugal speed has been shown to influence significantly the composition of the extracted soil pore water, which, depending on the specific soil considered, can display an effective increase in metal concentrations (Pérez *et al*., 2002).

3.3.3. Pressure filtering (Squeezing)

The squeezing method represents an approach where it is possible to modify the pressure during the extraction. This technique has been proved to be effective with various structured materials (coherent sediments and rocks) and has also been used for incoherent materials, including peat, clay, till, sand, silt, chalk, sea sediments (Entwisle and Reeder, 1983), but had never previously been used on soils.

The squeezing technique was originally developed to obtain pore water samples mainly from unconsolidated marine silts and clays. Manheim (1966) developed a heavy duty squeezer capable of applying a stress up to 150 MPa based on the early designs of a number of Soviet workers, most notably

Kriukov (1971). Similar designs have been used by Morgenstern and Balasubramonian (1980), Brightman *et al*., (1985), and Krahn and Fredlund (1972) to evaluate change in salinity with increased pore water extraction and increased pressure. The methodology has been used to extract pore fluid from materials with moisture content slightly below 7%. The method is often unsuccessful on highly cemented, hard material. In comparative studies, squeezing has been found to have a lower potential for contaminations and artefacts, partly because pore water extraction and filtration can be conducted in-line (Bufflap and Allen, 1995b). Very little direct contamination of the pore water resulted from clay studies using this extraction method (Entwisle and Reeder, 1993). In contrast differences in ionic strength and major components were found with increasing pressure applied and decreasing moisture contents (Cave *et al*., 1998, Reeder *et al*., 1998).

3.4. Materials and methods

3.4.1. Soil sampling and preparation

Soil sampling and preparation was the same as previously described (see section 2.5.1.).

3.4.2. Rhizon Samplers

3.4.2.1. Materials

Standard Rhizon samplers (Fig. 3.2) consist of a length of porous, chemically-inert hydrophilic polymer plastic (2.5 mm outer diameter, 1.4 mm inner diameter, average pore diameter ca. 0.1 µm), namely polyethersulphone (PES – G.P.J.P. van Dijk, pers. comm.). This is capped with nylon at one end, and attached to a 5 or 10 cm length of polyethylene tubing, with a Luer-Lock (L-L) male connector at the other end. The tubing is double walled, the inner sleeve is polyethylene (PE) because it is highly inert,

the outer wall (for strength) is polyvinylchloride (PVC). The porous polymer and part of the PVC tube is strengthened by a stainless steel wire. The Bubble Point (BP) of the sampler, i.e. the minimum pressure needed to overcome the capillary action of the fluid within the largest pores, which are then emptied[4], is greater than 200 kPa. The dead volume (or void volume i.e., the total of the volume of the porous material and the inner volume) is relatively low, ~0.5 ml.

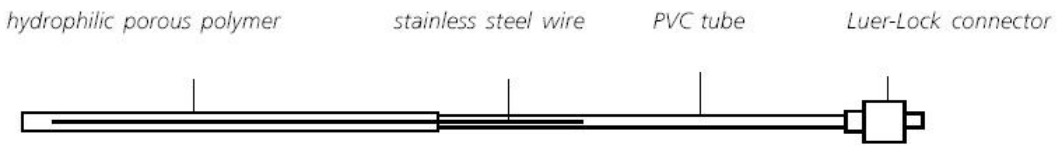


Figure 3.2. Sketch of a Rhizon sampler (from "Rhizon soil mosture sampler: operating instructions". www.eijkelkamp.nl).

3.4.2.2. Theoretical basis of method

When suction is generated within the sampling system, water is sucked inwards through the pores of the sampler until a corresponding capillary pressure occurs in the pores. If the capillary pressure in the sampler is lower than that in the soil, water flows from the soil into the sampler until the capillary pressure in the sampler and in the soil are equal. The maximum capillary pressure in a pore can be calculated by the following equation (Schubert, 1982):

$$p_c = \frac{-2\gamma(T)\cos\theta}{rgD_1} \times 10^{-9} \qquad (3.1)$$

where

[4] Bubble Point tests are usually carried out to characterize a membrane or porous material consistency or quality; they are also a common procedure to determine the maximum pore size.

p_c = capillary pressure (MPa);

γ = surface tension (N m^{-1});

T = temperature;

θ = contact angle;

r = radius of the pore (m);

D_1 = density of the liquid (kg dm^{-3});

g = gravitational constant (m s^{-2}).

This equation is valid for pores with a circular cross-section. For other shapes an empirical adjustment factor must be considered. Surface-active substances that are dissolved in the water, for example humic substances, can decrease the surface tension. Materials that are not completely hydrophillic (e.g. plastic) need a smaller pore size.

The time required for sampling depends directly on the actual unsaturated hydraulic conductivity (**k**) of a soil. Soil pore water will be extracted when **k** > 10^{-3} m day^{-1} and when there is a good hydraulic contact between the soil and the sampler.

3.4.2.3. Zone of influence

The zone of influence of the sampler is the zone where sampler installation and operation affect solute flow, the region of the soil from which rhizon water is drawn, and the fraction of soil water that is represented in rhizon solutions. The recharge area of these samplers (the space in which the water flows towards the sampler) depends upon the capillary pressure in the soil, the tension applied, the diameter of the sampler and the pore size distribution of the soil.

Warrick and Amoozegar-Fard (1977) presented an equation that theoretically described the maximum radius of influence (r_m). The former can be estimated in stationary conditions (steady state flow) for a point in an infinite medium around the sampler as follows:

$$r_m = \sqrt{\left(\frac{q}{\pi \cdot K_s}\right) \times 10^{(-\alpha \cdot h_1)}} \qquad (3.2)$$

where

q = volumetric flow rate into the sampler ($cm^3\ s^{-1}$);

K_s = saturated hydraulic conductivity ($cm\ s^{-1}$);

α = fitted parameter of hydraulic conductivity function (kPa^{-1});

h_1 = pressure head at r_m (outside the sphere of influence of sampler, kPa).

An alternative expression for the maximum radius of influence is that given by Morrison and Szecsody (1985), which was derived from equation (3.2) but with **k** (unsaturated hydraulic conductivity) expressed as a function of the hydraulic head (see also Hart *et al*., 1994 and Hart and Lowery, 1997):

$$k(h) = K_s^{(\alpha \Delta h)} \qquad (3.3)$$

where

$\Delta h = h_0 - h_1$

h_0 = suction head at the sampler (kPa)

Therefore r_m will be calculated as:

$$r_m = \sqrt{\left[\frac{4r_0}{\alpha} e^{\frac{\alpha r_0}{2}} \left(1 - e^{\alpha(\Delta h)}\right)\right]} \qquad (3.4)$$

where

r_0 = radius of the sampler

The constant α is empirically derived and is a measure of the relative importance of gravity and capillarity for water movement in the particular soil (see Bresler, 1978 and Morrison and Szecsody, 1985). Fine soils, where capillarity dominates, have small α-values; coarse soils where gravity effects control water transport have larger α-values (Phillip, 1968).

3.4.2.4. Pore water extraction

For the soil pore water sampling, the procedure described by Knight *et al*. (1998) and Tye *et al*., (2003) was followed. Four samplers were inserted into each of the soil containers. Soil pore water was extracted by connecting a syringe to each sampler and applying a suction. The zone of influence of the samplers was calculated according to equation 3.4.

3.4.2.5. Conditions of the porous material

Scanning Electron Microscopy (SEM) images and qualitative chemical analysis (EDX) of a brand new sampler, a used and acid-washed sampler and a used sampler, were taken to compare surface morphology, architecture and chemistry of the plastic porous material in pristine conditions and following pore water extraction (see section 2.5.3.5. for sample preparation).

3.4.3. Centrifugation

3.4.3.1. Materials

A Beckman J21C high-speed refrigerated centrifuge, fitted with a 6 x 500 cm^3 Beckman JA-10 fixed-angle rotor was used. Specially designed polyoxymethylene (Acetal) tubes provided with 316 stainless steel, 20 µm mesh filters were manufactured in-house to adapt the rotor available with the centrifuge (Fig. 3.3).

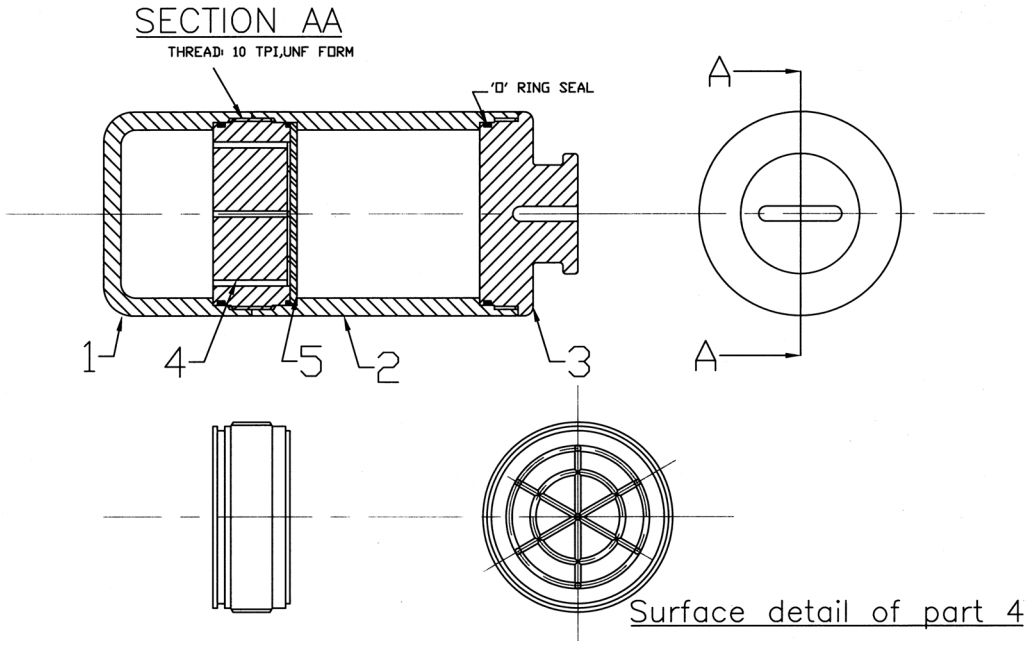


Figure 3.3. Centrifuge tubes for soil separation, designed and manufactured by R&D Workshop BGS, Keyworth; 1 – pore water collector cup; 2 – upper soil container; 3 – screwable acetal top; 4 – screwable acetal filter and support; 5 – stainless steel filter.

3.4.3.2. Theoretical basis of method

Although the exact force distribution is difficult to determine, the physics of fluid removal from porous geological materials by drainage centrifugation is fairly well understood (Edmunds and Bath, 1976). Given a column of soil under centrifugation, the tension applied, p_a, can be derived as:

$$p_a = \frac{\varpi^2}{2g}\left(r_1^2 - r_2^2\right) \tag{3.5}$$

where:

p_a = tension applied developed at a generic point r_2 of column (cm water);

ω = angular velocity (rad sec^{-1});

g = gravitational constant (cm s^{-2});

r_1 = distance from base of column to centre of rotation (cm).

The applied force is therefore a function only of distance from the rotor and the centrifugal speed, i.e. it has the same magnitude irrespective of the density and nature of the material tested, and the pattern of water removal will depend on the pore size distribution of the material. At equilibrium, p_a will be everywhere balanced by a capillary pressure, p_c, which can also be expressed as follows (Washburn, 1921):

$$p_c = \frac{2\gamma \cos\theta}{\rho \cdot r} \tag{3.6}$$

where

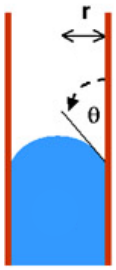
p_c = capillary pressure in a pore (N m^{-2});

γ = surface tension (N m^{-1});

ρ = specific gravity;

θ = contact angle between porous solid and liquid;

r = radius of pore (m).



The extent of interstitial water removal is therefore a function of the centrifuge dimensions and rotation speed, but it is also governed by the weight of sample used, the degree of initial saturation as well as the material's pore size distribution.

3.4.3.3. Pore water extraction

The centrifugation drainage procedure described by Edmunds and Bath (1976) and Gooddy *et al.*, (1995) was applied in the present study. The relationship between the distance to the centre of rotation and speed (hence pressure) applied was investigated for the supplied vessels and centrifuge rotor. The optimal choice of centrifuge speed, centrifugation time, and sample weight were also investigated in relation to the particular sample and volume of interstitial water required (see also Kinniburgh and Miles, 1983).

A known quantity of soil (at 5º C) was transferred into weighed centrifuge buckets. Samples were spun at the desired speed for 30, 45 and 60 min. Two speeds were chosen: 1500 and 7000 rpm, corresponding respectively to 39 and 858 kPa (equation 3.5). Upon completion, samples were removed from the centrifuge and the collection cups removed from each bucket. Dry bulk density was measured on the soil samples after centrifugation.

In these preliminary tests, any pore water extracted was collected using a disposable syringe, weighed and filtered through a 0.45 µm filter to mimic the procedure for the successive extractions prior to preservation for chemical analysis. If only small volumes of pore water were extracted, replicate samples were used to bulk the extracts. Distilled water blanks were passed through the extraction steps to minimize any contamination by materials or handling.

3.4.4. Pressure filtering (Mechanical squeezing)

3.4.4.1. Materials

The squeezing apparatus in use at BGS utilises a hydraulic pump (Wykeham Farrance Engineering Ltd., Slough) which has a maximum output stress of 70 MPa and hydraulic hoses and fittings (Fig. 3.4). The main body of the cell and other metal parts in contact with the test sample or pore water are manufactured from Type 316 stainless steel, which was selected because of its resistance to corrosion and its high tensile strength.

The cell body sample chamber is 75 mm in diameter and 100 mm high (Fig. 3.5). The outside of the cell has a spiral trough through which temperature controlled fluid circulates inside a plastic insulation jacket. Temperature control of the cell is achieved by a heater/chiller, which is capable of temperature control between -10° and 50°C. The pore water collection pipe screws into the top plate. Pore fluid is collected directly into disposable polypropylene syringes.

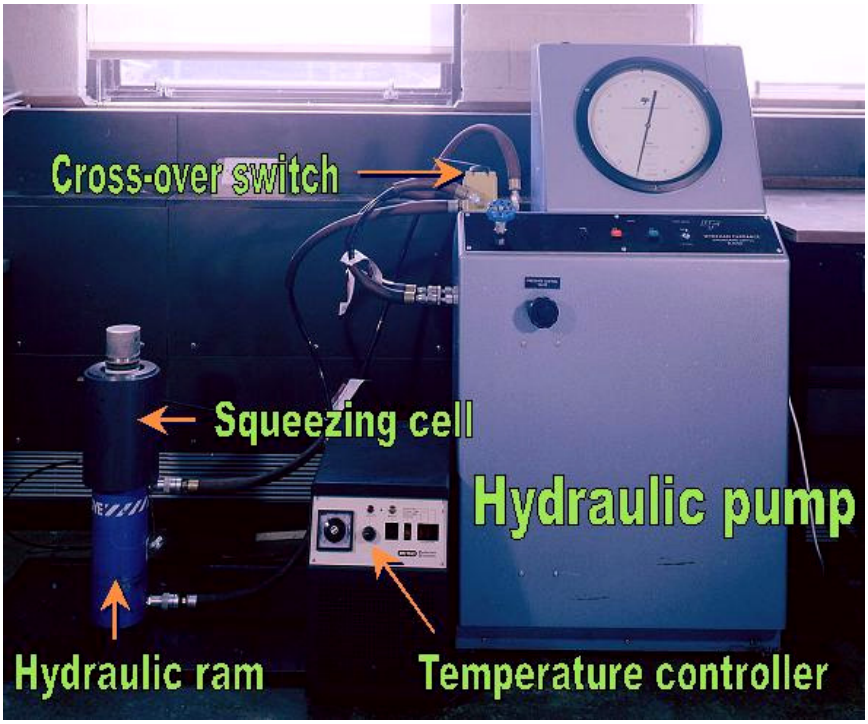


Figure 3.4. Squeezing apparatus, designed and manufactured by R&D Workshop, BGS Keyworth.

Figure 3.5. Clay squeezing cell, designed and manufactured by R&D Workshop, BGS Keyworth.

Two syringe taps (which can have a 0.45 μm Acrodisc filter in between) are pushed onto the pore water pipe allowing flexibility of pore water collection: taps can be opened and closed when multiple samples are collected and syringes need to be replaced. The metal filter, which has a diameter of 90 mm, is also made of Type 316 stainless steel (see Entwisle and Reeder, 1993 for further details).

3.4.4.2. Theoretical basis of method

The squeezing process involves the expulsion of pore water from the material being compressed. In general the material consists of solid particles (mineral phase), and spaces (voids), which in an unsaturated environment such as a soil, contain both air and water. When a squeezing stress is applied to a water-saturated material, its volume decreases by three main mechanisms:

- compression of the solid phase;
- compression of the pore water between the solid phase; and
- escape of water from the voids.

In most circumstances, the compression of the solid and liquid phases is negligible and most of the change in volume is caused by the escape of pore water. This may be illustrated by a hydromechanical analogy for load changing and squeezing as shown in Figure 3.6 (after Lambe and Whitman, 1979). The resistance of the solid phase during compression is represented by a spring and the rate at which the pore fluid flows is dependent upon the size of the valve aperture. In (a) the valve is closed and in equilibrium. When a pressure is added (b) the piston load is apportioned by the water and the spring in relation to the stiffness of each. There is little movement in the piston because the water is relatively incompressible. Most of the load is carried by the water and this increases the water pressure. If the valve is now opened (c) the excess pore pressure dissipates by water escaping through the

valve (d). The piston drops and the volume of the chamber decreases until there is a new equilibrium when the applied load is carried by the spring and the water pressure has returned to the original hydrostatic condition (e). The gradual transfer of load from the water to the spring is shown in (f). The dissipation of the pore water is called primary consolidation.

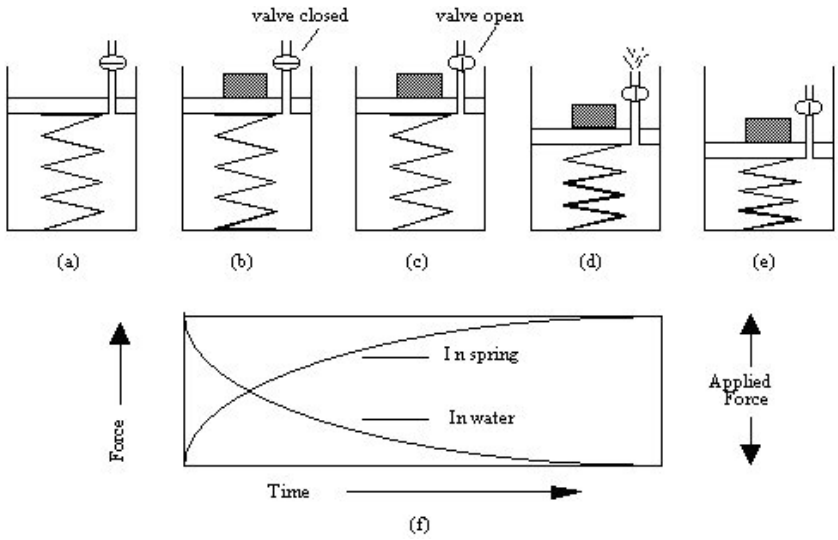


Figure 3.6. A hydromechanical analogy for load changes during squeezing (after Lambe and Whitman, 1979).

The rate at which the pore fluid is expelled is related to the length of the sample and the pore size. A typical graph of the rate of settlement, and therefore pore fluid extraction, after the addition of a load (Fig. 3.7) shows both primary and secondary consolidation.

Most of the excess pore pressure dissipates during primary consolidation. Secondary consolidation involves the movement of particles as they adjust to the increase in effective pressure and the dissipation of excess pore pressure from very small pores. The pore water extracted during squeezing is mainly due to primary consolidation.

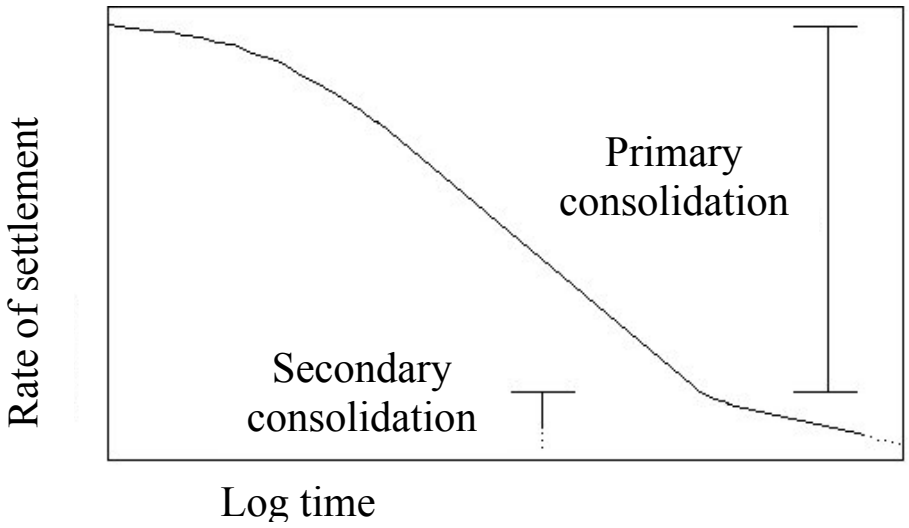


Figure 3.7. The rate of settlement for increasing stress (modified, from Entwisle and Reeder, 1993).

3.4.4.3. Pore water extraction

Since this method had never been used for soils before, three soils (Hp, Np and SB) with different texture and characteristics were tested on the squeezing apparatus to assess the rate of release of pore water.

The soil was placed into the clean dry cell. A 90 mm diameter Whatman filter paper was then placed on to the shoulder of the sample chamber and a clean steel filter placed on top of the filter paper. The top plate is screwed into the cell to contact the metal filter; the temperature control unit cooler was then switched on. A small nominal stress (<1 MPa) was applied to remove most of the air from the cell and to allow the sample and the components to bed in. When the selected temperature (±2°C) was attained, the pressure was increased and water collected. A temperature of 15°C was chosen to match the temperature of the conditions of soil storage.

The squeezing test may take from 1 hour to in excess of 2 or more weeks, depending on the set up and the physical properties of the material, producing either a single bulk sample or a number of "sequential" water samples (Ross *et al.*, 1989). Sequential extractions were used here in order to

assess the release of pore water, analyse the samples separately, and study the change in composition with progressive pore water extraction.

When sufficient volume of pore water had been obtained (~ 15 mL to allow chemical analysis), the syringe was removed and the sample filtered as soon as collected through a 0.45 μm Nylon Acrodisc Syringe Filter (Pall-Gelman - HPLC certified). Filtered samples were poured into 15 ml Röhre tubes (Sarstedt) and sub-samples of each syringe were acidified to 1% v/v (Aristar HNO_3) for ICP analysis. Further fractions of sample were collected by continued squeezing, using a new syringe assembly, until no further pore water could be obtained (Cave *et al*., 1998).

After the test was completed, the squeezed sample was removed from the cell and the apparatus dismantled and cleaned. The test specimen was measured to calculate its volume, weighed and oven dried at 105°C for density and moisture content determinations.

3.4.5. Extraction Efficiency

Duplicate samples of the soils tested were taken at the same time as the sample was prepared for both centrifugation and squeezing extraction, for the determination of moisture content. Moisture contents determined as part of centrifugation and squeezing extraction tests are normally reported with respect to the dry weight. A known mass (at least 50 g, in triplicates) of the original sample was tested by determining its weight before and after heating at approximately 105 to 110°C for a minimum of 24 h.

The percentage moisture content with respect to the initial wet sample weight, θ_w, was determined as:

$$\theta_w = \frac{W_w - W_d}{W_d} 100 \tag{3.7}$$

where

W_w = wet sample weight;

W_d = dry sample weight.

The percentage of the available pore water extracted, E, (Entwisle and Reeder, 1993) was determined as:

$$E = \frac{W_p}{W_{si} - W_{sd}} 100 \tag{3.8}$$

where

W_p = weight of pore water collected;

W_{si} = weight of sample initially tested;

W_{sd} = weight of sample post squeezing (centrifuging) after oven drying.

This can be written as:

$$E = \frac{W_p}{W_s \cdot \theta_w} 1000 \tag{3.9}$$

where

θ_w = moisture content with respect to initial wet sample weight.

3.4.6. Chemical analyses on pore waters

pH was determined on all squeezed pore water samples as soon as possible after collection using a standard pH meter provided with a 4 mm leadless micro electrode. Major cations (Ca, K, Mg, Na), trace elements (B, Ba, Be, Cu, Fe, Mn, Ni, Si, Sr, Zn) and total P and S were determined by ICP-AES, using a Fisons/ARL 3580 spectrometer. Further trace elements (Al, As, Li, Cd, Co, Cr, Cs, Cu, Mo, Ni, Pb, Sb, Sn, U, V and Zn) were also determined using a Thermoelectron VG Elemental Excell ICP-MS spectrometer. Analyses were carried out on 5 ml of sample acidified to 1% v/v with respect to Aristar HNO_3. Major anions (Cl, NO_3, SO_4, HPO_4) were determined by Ion Chromatography (DIONEX DX600). A Shimadzu TOC-5000 total organic analyser fitted with ASI-5000 autosampler was used to determine total organic and inorganic carbon (DIC and DOC) using 5 ml of un-acidified sample. All the elemental analyses were performed at the BGS, in laboratories operating under UKAS Accreditation for natural waters

(including pore waters, synthetic fluids, hydrothermal fluids and aqueous leachates).

3.5. Results and discussion

3.5.1. Rhizon samplers

Nominal data for physical characteristics and dimensions of the Rhizon samplers are given in Table 3.1.

Table 3.1. Physical characteristics and dimensions of a Rhizon sampler.

q	BP	Porous area	Length	Internal diameter	Outer diameter	Internal Volume	Dead Volume
$m^3\ s^{-1}$ (10^8)	kPa	cm^2	cm	cm	cm	cm^3	ml
1.7	200	7.90	10	0.14	0.25	0.15	0.5

BP: Bubble point

According to the supplier (Eijkelkamp, www.eijkelkamp.nl), a Rhizon sampler with 10 cm length porous polymer producing a 7 ml sample, will have removed a water cylinder of 1 cm diameter. Following this approach, it was concluded that a generic zone of influence, extending to a radius of 5 cm in all directions from the edge of the porous sampler, should be considered. The assumption of a 5 cm radius of influence however is not supported by any consideration of properties such as hydraulic conductivity or porosity and was only to advise users to space samplers at 5-10 cm distance between each other.

Alternatively, the maximum radius of influence, r_m, can be calculated using equations (3.2) and (3.4). Figure 3.8 shows r_m as calculated by equation (3.4), varying the pressure head (Δh) and the type of soil (α-value). The real diameter of a Rhizon sampler and optimal sampling conditions (h_0 = -200 kPa) were assumed for the calculations. The two vertical lines, FC (Field

Capacity) and 'syringe suction', enclose the expected conditions for any soil in this study. According to Cabrera (1998), 10 ml plastic syringes applied to Rhizon samplers are likely to generate an average suction of -48.1 ± 0.5 kPa.

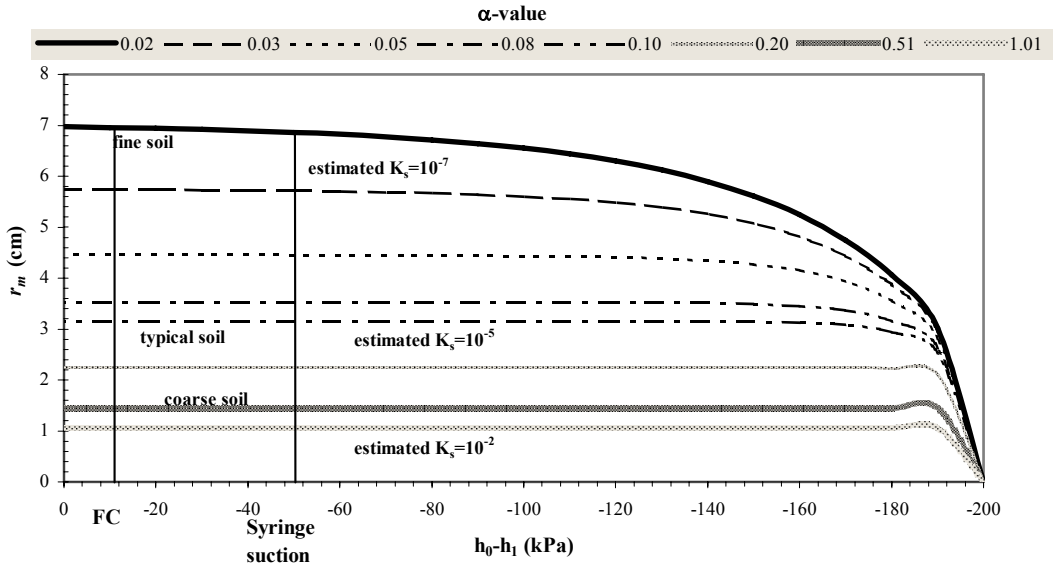


Figure 3.8. Radius of influence of a Rhizon sampler as a function of the pressure head and the soil type.

As expected, the radius of influence is greater for finer (clayey) soils, and smaller for coarser soils. The radius for the Stoke Bardolph soil falls between 4 and 6 cm. In addition, within the studied conditions, the radius does not seem to be significantly influenced by the pressure head. This was not measured for the present study as the purpose was to work with an unsaturated soil at FC.

The α-values shown in Fig. 3.8, range through most of the published α-value for soils (0.01 kPa^{-1} to 1.01 kPa^{-1}). However, there is a considerable variation in α and K_s, therefore more accurate r_m calculations can be made if those two parameters are determined experimentally for a particular soil.

In general, the calculation showed that the overall axial-radial influence of this type of sampler is very small, confirming the findings of Hart and Lowery (1997). This could result in a limitation of the method especially

when the soil is not homogeneous (or it has not been homogenised) causing preferential flow conditions to prevail.

Samples collected with these devices may inadequately represent the pore water in its natural occurrence because of problems inherent in the technique (Litaor, 1988). This limitation may be additionally influenced by the complex nature of the soil, whose heterogeneity highly affects the chemical concentrations in pore water. Hence rhizon samplers, with their small cross-sectional area, may not adequately integrate for spatial variability (England, 1974; Amoozegar-Fard *et al*., 1982; Haines *et al*., 1982), and may represent 'point samples' with qualitative rather than quantitative attributes (Biggar and Nielsen, 1976).

Examination of the Rhizon samplers by SEM (Fig. 3.9) shows detail of the external surface of a pristine sampler. This clearly shows the porosity and the distribution of the pores through which the solution will be withdrawn from the soil sample. The spectrum of the chemical composition shows that the material forming the samplers is organic, with peaks of C, O and S, as one would expect considering that the porous part of the sampler is made of PES. The presence of Au is due to the sample preparation, during which the sample is coated in gold. Figure 3.10 shows the external surface of a sampler that has been used several times for extraction, and cleaned with a slightly acid solution (5% volume HNO_3). For comparison, images from the two samplers were recorded at identical magnifications. The 'used' sampler appears to have no remnant porosity, or anything resembling residual pore structure. The EDX spectra show no significant compositional differences between the 'pristine' and the 'used' sampler. The only elements present are C, O, and S with approximately similar peak intensities. Arguably the external surface is coated with some organic layer which does not alter the overall chemical composition shown by the EDX spectrum.

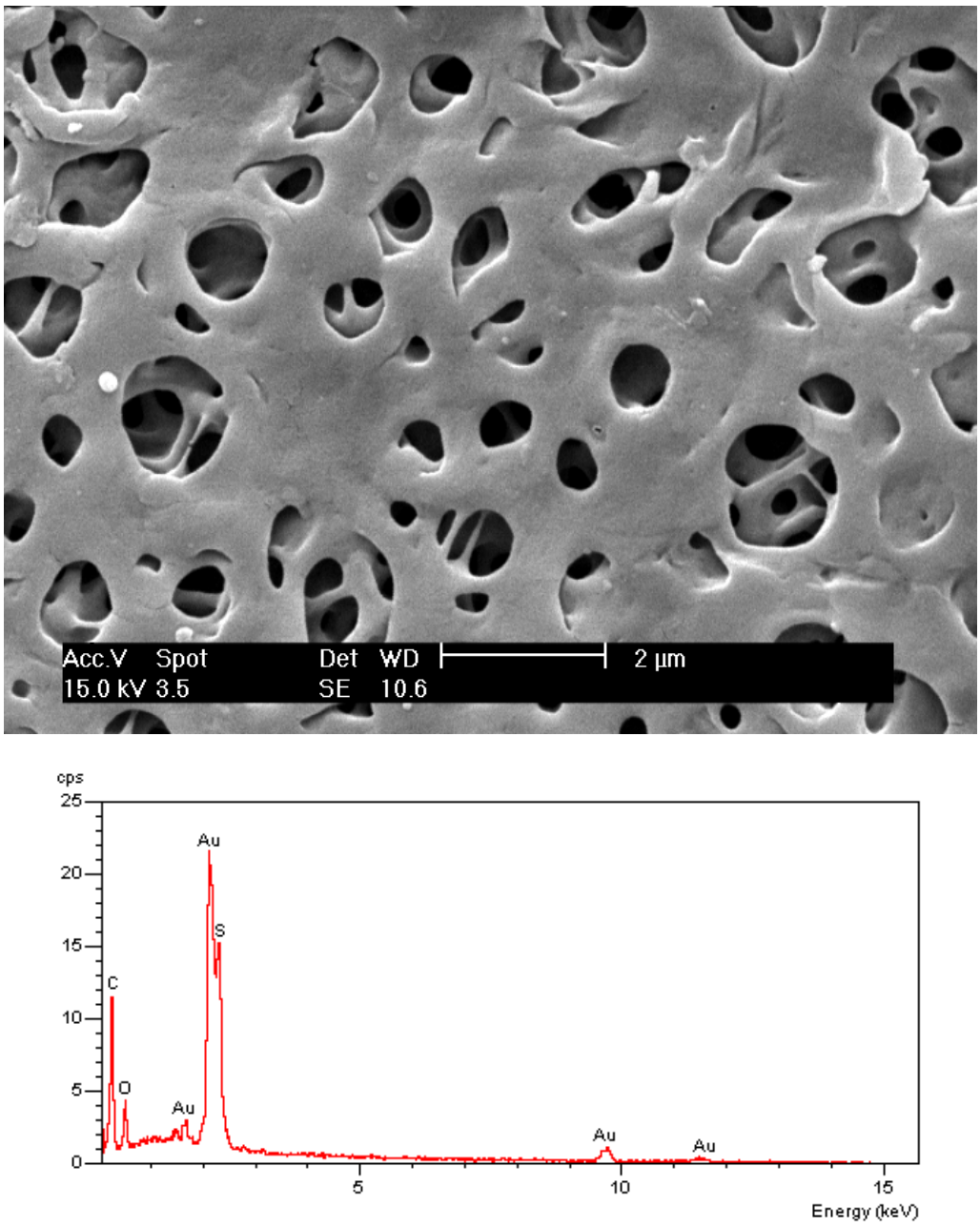


Figure 3.9. Secondary electron micrograph image and EDX spectrum of elemental chemical composition for an Au coated 'pristine' Rhizon sampler.

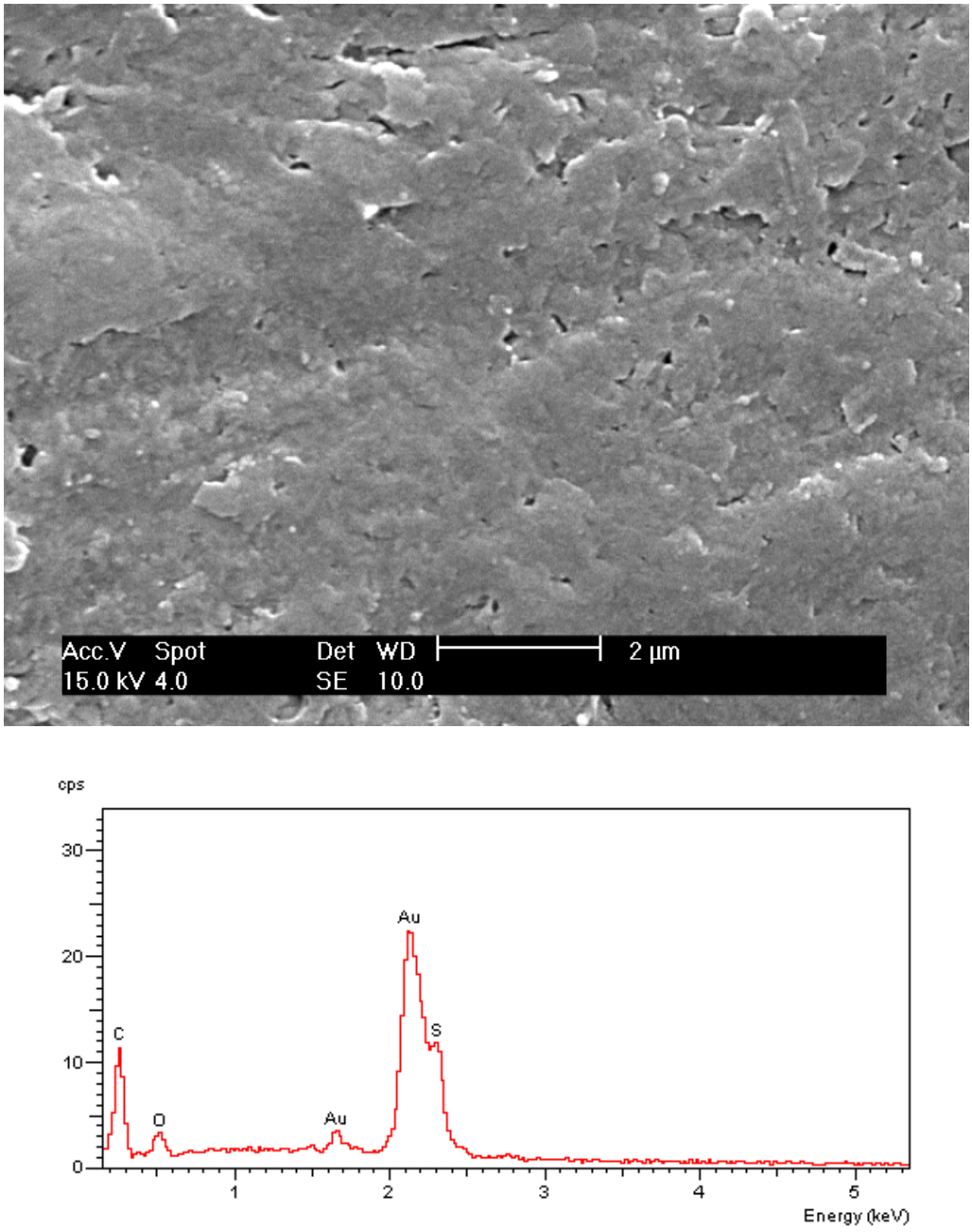


Figure 3.10. Secondary electron micrograph image and EDX spectrum of elemental chemical composition for an Au coated 'used and washed' rhizon sms.

If an organic layer (e.g., humic acid) were forming on the outer surface of the samplers, this would probably have a significant cation exchange capacity. The acid-washing stage of cleaning the Rhizon samplers would protonate such surface coatings. The resulting pool of exchangeable H^+ ions would be unaffected by subsequent washing with deionised water. Ion

exchange between Rhizon-H^+ and soil pore water cations would acidify the extracted pore water, causing major alterations in the pore water speciation.

Alternatively, the loss in porosity could be the product of a mechanical stress on the surface of the sampler, which is subjected to pressures from the soil when this is compacted by the installation process and the suction consequently applied. Observations of SEM pictures do not clarify this point, or whether there might be a combination of the two processes leading to the loss of porosity. It is a fact that after 3-4 uses (Andrew Tye, pers. comm.) the suction performance of the sampler decreases significantly, raising questions about the life expectancy of the material itself. Naturally this depends on the conditions to which we subject the rhizon samplers, from soil at different acidity, organic matter, clay and moisture content. The material is fairly resistant to acid attack, but the same cleaning operation executed several times may damage and alter the material.

3.5.2. Centrifugation

During centrifugation a soil sample is spun at a specific speed, which corresponds to a relative centrifugal force (RCF) and, according to equation (3.5), a corresponding pressure. The pressure on each point within the soil column can be represented depending on the distance to the axis of rotation and speed. Fig. 3.11 shows the variation of the applied pressure within a single bucket, as calculated by using equation (3.5). The radius varies between 5 (top of the column) and 9 cm (base of the column) depending on the position of the point inside the bucket, which is inclined at 45^o with respect to the axis of rotation. In this situation we considered the maximum speed achievable as ca. 7000 rpm, which was calculated according to a reduction factor for the rotor in use with the centrifuge, in case of materials having density higher than water (Beckman instruments, 1988).

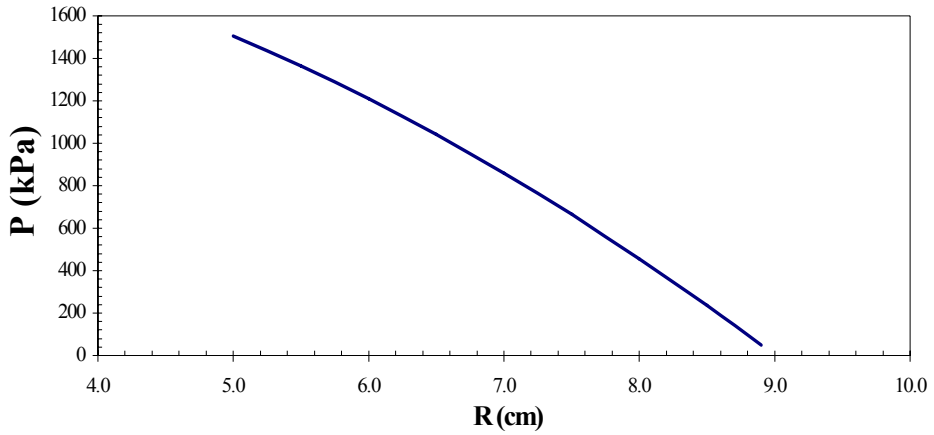


Figure 3.11. Pressure profile depending on distance R from rotation axis at maximum speed (7000 rpm) based on equation (3.5).

The mean distance from the axis of rotation is 7 cm, which is the midpoint at which we can calculate the relationship between the varying speed and the pores drained according to equation (3.6). Fig. 3.12 shows the resulting pressure profile at the midpoint with varying centrifugal speed.

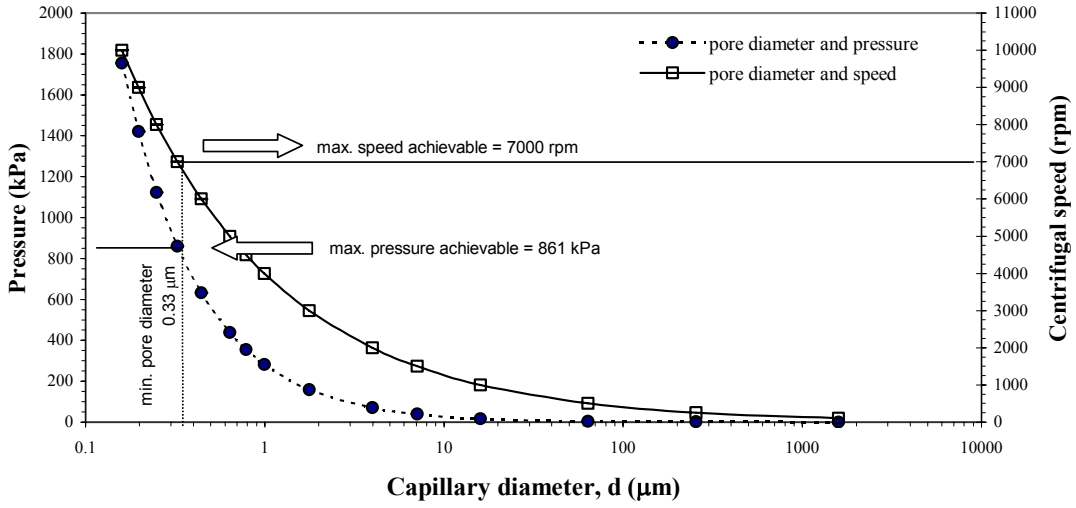


Figure 3.12. Pressure profile depending on the speed at a midpoint of 7 cm from axis of rotation calculated using equation (3.6); relationships between speeds of rotation, pressure applied and minimum capillary size drained (radius = 7 cm).

The highest speed achievable corresponds to ca. 860 kPa; at this pressure the smallest capillary pore that can in theory be accessed is 0.33 μm in diameter. This corresponds to the class of pores defined as **residual**. Above 0.5 μm (corresponding to a speed of ca. 6000 rpm, equal to 632 kPa) and up to 50 μm we are accessing **storage pores**. Therefore, with the centrifugation method in principle we are able to access these two different ranges of functional pores, both classified as mesopores (see table 2.3).

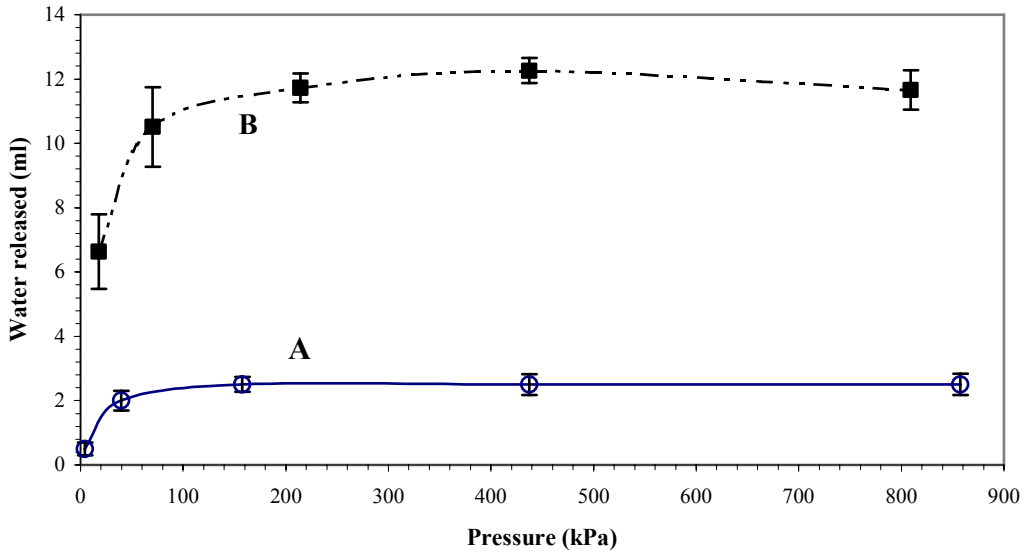


Figure 3.13. A) Release of pore water with increasing speed (converted to pressure) for the Stoke Bardolph soil using 86 g of soil at 5° C and FC conditions; B) release of pore water during the experiment conducted in real conditions (greater mass of soil, same temperature and FC conditions, see Chapter 4); vertical bars represent standard errors.

Tests were also conducted to verify the release of water with varying time and centrifugal speed. Fig. 3.13 shows the relation between relative volume of water released and pressure applied during centrifugation. It appears that the release of water reaches a maximum peak in correspondence of ca. 160 kPa (3000 rpm). Subsequently the release of water does not vary significantly, approaching a steady state-like behaviour. This could be due to an initial release of more mobile water and higher moisture content, followed

by the release of less mobile water from smaller and less accessible pores and lower moisture content. In the simplest case of piston and preferential flow (Beven, 1989), water is considered to have a bimodal distribution in velocity, corresponding to 'mobile' and 'immobile' phases (Coats and Smith, 1964). In an unsaturated soil medium with a given degree of heterogeneity, piston flow tends to be dominant at higher water contents and preferential flow at lower water content (Padilla *et al*., 1999).

The volume of solution extracted is a function of the initial weight of the sample, the pore size distribution (PSD) of the soil, the degree of initial saturation, the centrifuge dimensions, and rotational speed (Edmunds and Bath, 1976).

Fig. 3.14 shows the yield of pore water at two different centrifugal speeds after different durations of centrifuging. The volumes of water extracted are consistent with the idea that at higher speed we can access a broader range of pores from which to withdraw soil pore water.

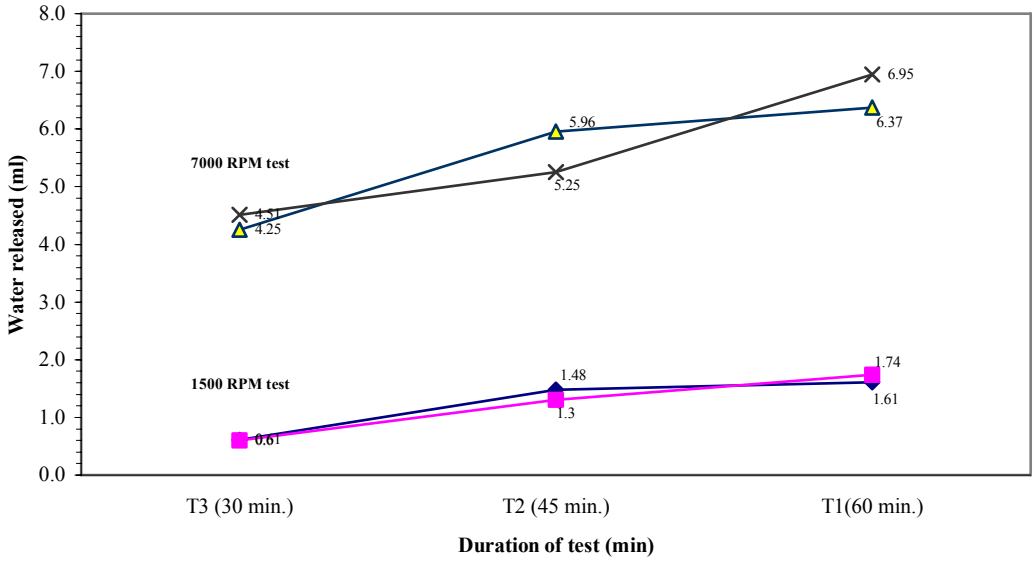


Figure 3.14. Release of pore water from Stoke Bardolph soil with increasing duration of centrifuging. Initial conditions: 5° C, 86 g soil at FC.

This can be also compared with the water released at 6000 rpm (~ 631 kPa matric suction, corresponding to 0.23 µm pore diameter) with time shown in Fig. 3.15. At the studied conditions, the release of water reaches a plateau after the 8th hour of extraction. Cumulative water extracted during centrifugation can be predicted for our conditions with a nonlinear regression analysis: this is showing a good fit ($P < 0.01$) with an equation of the type:

$$y = A + B \cdot R^x \tag{3.10}$$

where x is the Time (t) in min. and other parameters are defined in Table 3.2.

Table 3.2. Estimate of parameters for equation 3.11 for predicting the release of water with time.

Parameter	Estimate	Standard Error
R	0.99041	0.002
B	-7.143	0.407
A	8.781	0.517

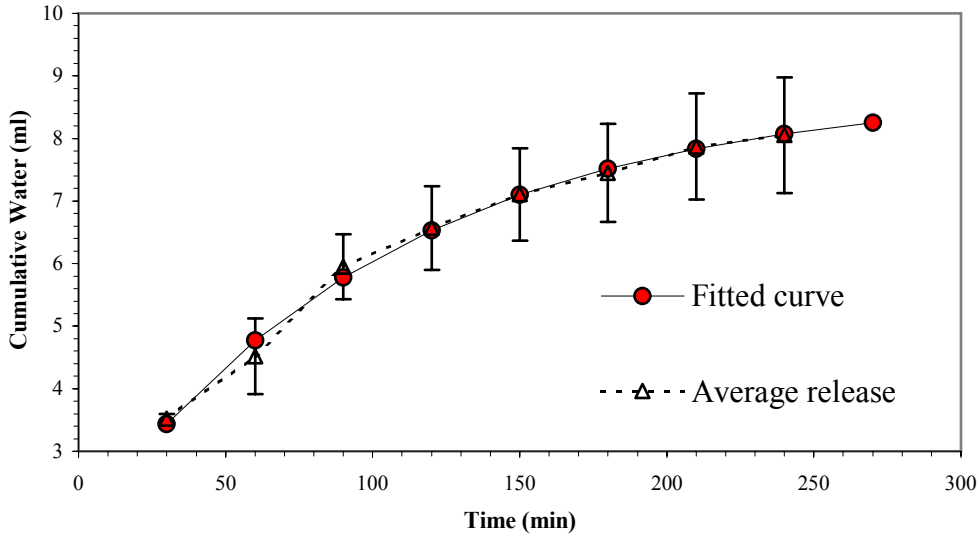


Figure 3.15. Cumulative water released by centrifugation at 6000 rpm (631 kPa) as a function of time. Solid line represents a predicting function (logarithmic); vertical bars represent standard errors.

During centrifugation compaction of the soil occurred. From an initial bulk density (ρ_b) of 0.67, a final ρ_b of 1.01 was measured. Although this is a predictable drawback of the methodology, it could lead to misinterpretation of the possible sources of the water in terms of porosity if not carefully considered. According to Jones and Edwards (1993), a moisture content gradient also develops through the sample. As water migrates down through the sample, the base of the soil, from which the solution is released, will be in excess of its water-holding capacity (0 kPa) during part of the centrifugation process.

Centrifugation achieved an efficiency of 28% (measured on a single tube), and very little pore water was collected at low speeds (1000 and 2000 rpm). This is due to the initial moisture content of the soil used and the low pressure differential between the matric potential of the soil (representing the strength at which water is held in the soil), equivalent to FC (-10kPa), and the corresponding potential applied during these steps (respectively 18 and 70 kPa). When centrifuging, pore water is lost from the sample when positive pressures exerted by centrifugal force are greater than the matric suctions exerted by the solid phase (Jones and Edwards, 1993). A significant amount of water (40% of the total) remained in the samples at the end of the 5-step centrifugation extraction (Fig. 3.16). Furthermore, the change in bulk density occurring during centrifugation affects the nominal pore distribution. As a result, the release of water does not follow the theoretical curve based on the moisture characteristic, raising questions about the correlation between pore water released at specific pressures and the corresponding pore size. It has to be stressed however that the moisture characteristics is built on a series of equilibrium stages, whereas the water is released during centrifugation in steps of an arbitrary duration (1 h), which are not necessarily achieving equilibrium.

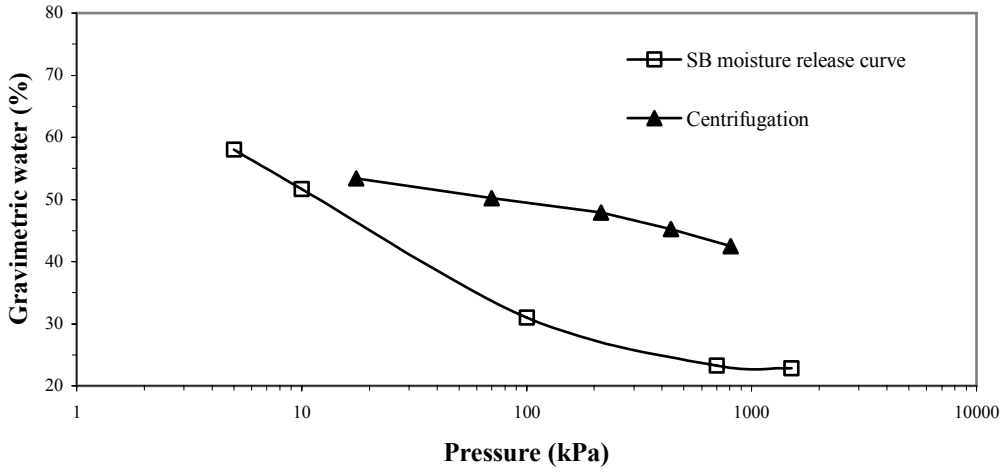


Figure 3.16. Percentage of water remaining in Stoke Bardolph soil during centrifugation. Centrifugation was performed in 5 steps: 18, 70, 214, 438 and 809 kPa (converted to pressures from rpm: 1000, 2000, 3500, 5000 and 6800); initial water content: 84.7 g (56% moisture content, DWB); water extracted: 62.4 % of total content; moisture content at the end of the run: ca. 40 % (DWB).

3.5.3. Soil squeezing

General information about the squeezing tests is summarised in Table 3.3. Stoke Bardolph (SB), Newport (Np) and Hanslope (Hp) produced respectively 10, 2 and 12 pore water samples, each one of about 13 ml volume. The weight of extracted pore water was 131 g for SB, 21.4 g for Np and 181 g for Hp. The extraction for Np was not completely successful due to mechanical failure and soil intrinsic texture.

Extraction efficiency, $\%E$, for the three soils were calculated. For Np, $\%E$ was 27.4%. This is due to the initial low moisture content (11.1%) and the sandy texture of the soil. Previous tests on different materials (Entwisle and Reeder, 1993) showed that samples with an initial moisture content of less than 10% present a low extract efficiency and that there is an apparent cut-off of about 7-8% below which no water is collected. Furthermore, the sandy texture of the soil suggests that solid particle repacking, which is one of the main mechanisms through which pore water is displaced, will be limited

during squeezing. The rate of settlement and therefore the pore water extraction by primary consolidation are also related to the change in volume (i.e., voids ratio) that the sample suffers during the process; this is related to the texture of the sample, with sand giving lower porosity (void ratio calculated at the end of the test = 0.58). $\%E$ for SB and Hp were 68.3% and 67.4% respectively.

Table 3.3. Summary of condition used for squeezing soil samples.

Sample	Test time (h)	Total time (h)	Pressure (MPa)	Mass extracted (g)	Total mass extracted (g)
			Stoke Bardolph		
sb1	0:30	0:30	0.50	14.4	14.4
sb2	2:05	2:35	0.55	14.9	29.3
sb3	19:25	22:00	0.65	9.20	38.5
sb4	28:00	50:00	0.95	12.8	51.4
sb5	48:50	98:50	2.00	14.2	65.5
sb6	46:00	144:50	3.40	13.3	78.8
sb7	45:30	190:20	8.00	16.1	95.0
sb8	48:00	238:20	18.0	14.8	110
sb9	105:00	343:20	42.0	15.4	125
sb10	474:00	817:20	49.0	5.31	131
Date squeezing started		21/06/2000		Initial sample weight	540 g
Minimum pressure		0.5 MPa		Maximum pressure	49 MPa
			Newport		
np1	195:30	195:30	36.0	13.0	13.0
np2	475:30	671:00	60.0	8.36	21.4
Date squeezing started		28/06/2000		Initial sample weight	700 g
Minimum pressure		0.75 MPa		Maximum pressure	60 MPa
			Hanslope		
hp1	27:30	27:30	0.70	14.4	14.4
hp2	19:30	47:00	0.70	15.2	29.5
hp3	10:00	57:00	1.00	14.7	44.2
hp4	16:00	73:00	1.00	13.8	58.0
hp5	30:00	103:00	1.00	14.9	72.9
hp6	26:20	129:20	1.20	14.8	87.7
hp7	46:00	175:30	1.40	13.4	102
hp8	86:30	262:00	2.00	17.9	119
hp9	246:30	508:30	4.00	15.3	134
hp10	211:30	720:00	8.60	15.4	150
hp11	216:00	936:00	27.0	15.5	165
hp12	673:30	1609:30	69.0	15.5	181
Date squeezing started		28/06/2000		Initial sample weight	720
Minimum pressure		0.3 MPa		Maximum pressure	69 MPa

The time taken to complete the tests varied from 671 hours for Np to 1609 hours for Hp. The times required to collect individual solution samples are also reported; this information is compared with the maximum pressure applied during the extraction to assess the test conditions for each soil. When the moisture content decreased, the clayey soil (Hp) required higher pressures for a longer time (see Table 3.3) to produce the required mass of water. In general, stiffer materials of low permeability require longer periods of squeezing.

Problems were experienced with SB and Np soils. These tests were stopped because it was not possible to increase the pressure further; the hydraulic pump did not achieve more than 49 MPa for SB and 60 MPa for Np.

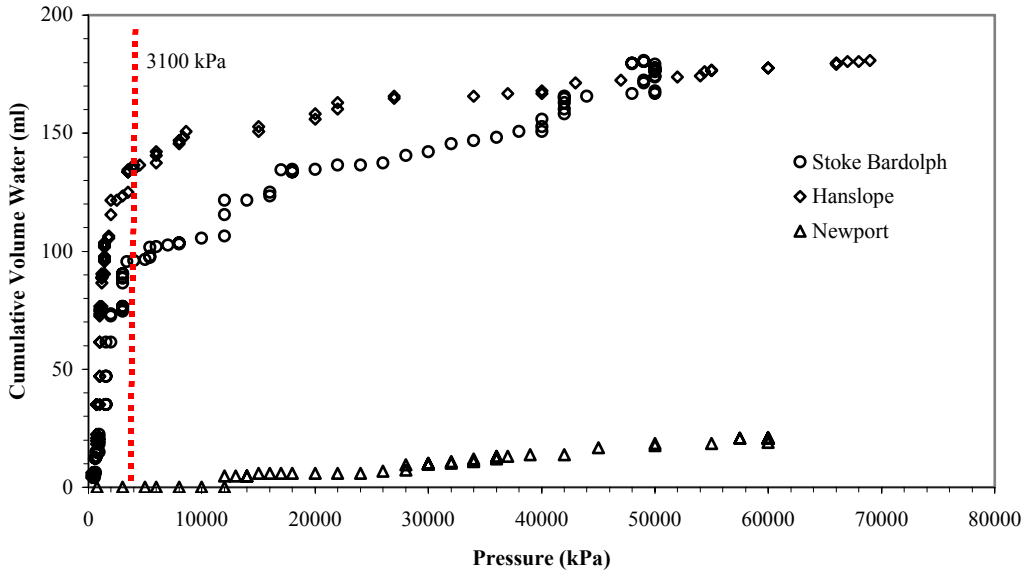


Figure 3.17. Cumulative volume of pore water extracted for the three soils tested with increasing pressure; the dotted line represents the pressure corresponding to the hygroscopic coefficient, i.e. the upper limit for the capillary water.

Figure 3.17 shows the cumulative release of pore water for the three soils tested. The dotted line represents the pressure corresponding to the

hygroscopic coefficient, i.e. the upper limit for the capillary water. This illustrates the capability of squeezing to reach a wider range of pores. This pressure value should also correspond to most of the available water in the soil. In fact by this stage almost 75% of the total water was extracted for Hp and 60% for SB.

Soil compaction was clearly very marked for Hp and SB and to a lesser extent for Np (Table 3.4), due to the soils intrinsic characteristics.

Table 3.4. Summary of water yields and physical parameters during the squeezing tests for the three soils studied; θ = moisture content (initial and final); W = mass of solid (f = final wet, d = dry).

Soil	θ_i %	θ_f %	W_f (g)	W_d (g)	Total H_20 (g)	H_2O available (g)	Efficiency (%)	Density (g cm^{-3})	Voids ratio	Porosity
SB	53.2	9.04	381	349	131	213	68.3	1.80	1.34	0.57
Np	11.1	7.26	667	621	21.4	77.7	27.4	2.21	0.58	0.37
Hp	43.1	6.70	483	452	181	310	67.4	2.20	1.17	0.54

Preliminary chemical analyses were also carried out on the sampled pore water and some results for selected metals as well as carbon and pH are shown in Figures 3.18 and 3.19.

There is evidence of composition variability with increasing pressures. Trace metals show a general decrease in concentration with subsequent extractions for Stoke Bardolph (with the exception of the final tail for Ni). For Hanslope As and Ni seem to increase with increasing pressure applied, with Zn increasing and then decreasing from Hp8 (2000 kPa). Similarly, organic and inorganic C vary across the samples, which suggests that the effect of the increasing pressure requires further investigation.

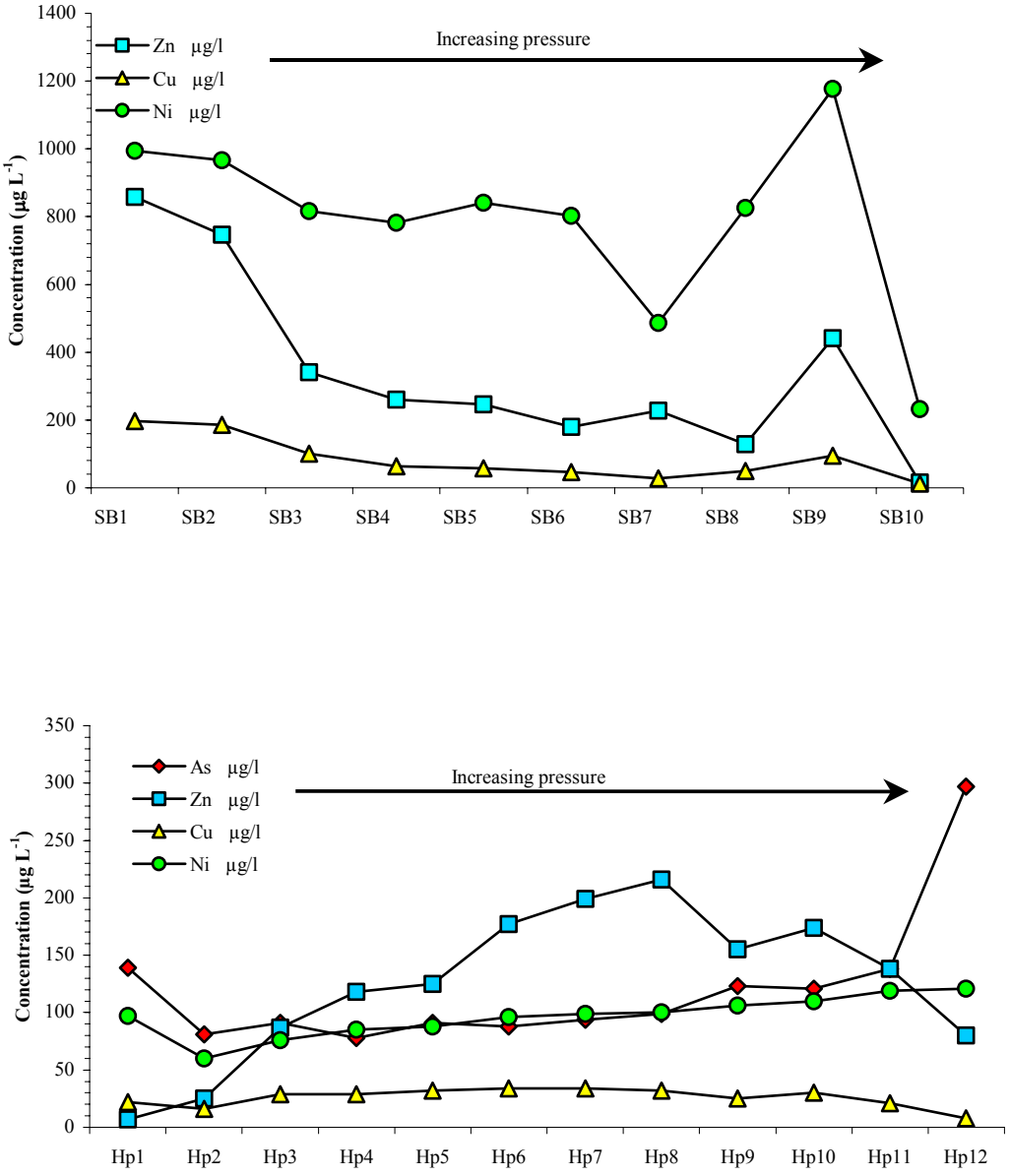


Figure 3.18. Selected trace metals composition for the pore water samples extracted by squeezing for a) Stoke Bardolph and b) Hanslope soils.

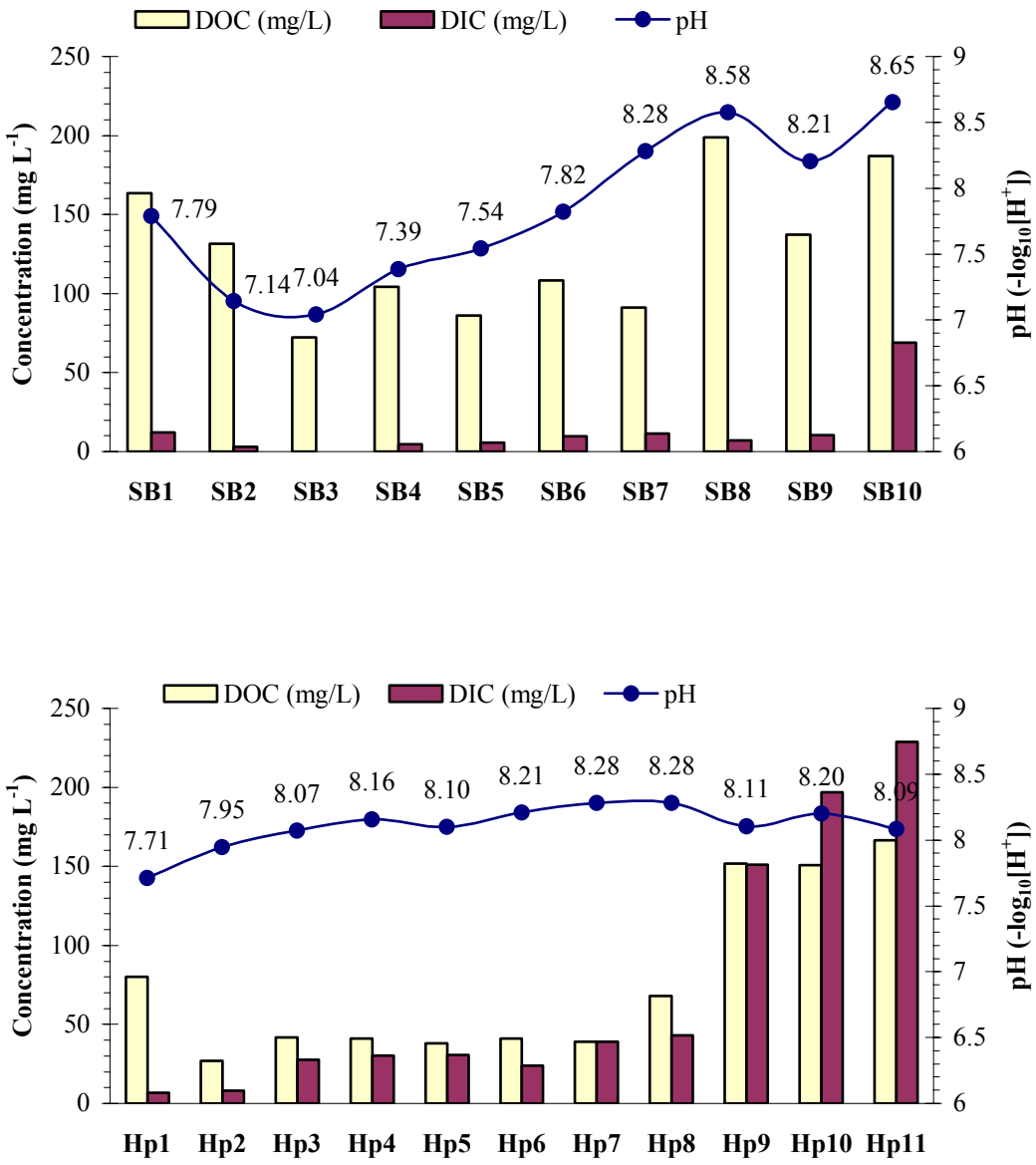


Figure 3.19. Organic, inorganic carbon and pH composition for the pore water samples extracted by squeezing for a) Stoke Bardolph and b) Hanslope soils.

3.6. Conclusions

Rhizon samplers, centrifugation and squeezing were operationally tested for pore water sampling. An alternative way to measure the radius of influence of Rhizon samplers was suggested by the application of previously

tested equations. Results show that the overall geometric mean axial-radial influence of these samplers is very small, suggesting careful consideration of the samplers' placement and experimental designs as a function of the characteristics of the soil to be studied are required. Rhizon soil moisture samplers will only function when the soil is not too dry, i.e. when the matric potential is greater than 10 kPa (above FC) and the potential gradient and the hydraulic conductivity are too low to obtain a sample. Rates of solution accumulation by tension samplers can vary in a given soil due to heterogeneity of moisture content and solution flow pathways. Increasing the applied tension increases the non-uniformity of sampling. Hence the more uniform the particle size the more uniform is the sampling rate. Furthermore, although the manufacturer claims the material that makes these devices is chemically inert, the problem of possible adsorption and/or chemical reactions on the surface is still present and need to be addressed. Perhaps Rhizon samplers are best used as a 'one-time-only' (i.e. disposable) option, otherwise careful consideration has to be made about the porosity and the suction capacity of the material.

Centrifugation covers for a wider range of pore sizes compared to Rhizon sampling, but nevertheless will only yield a fraction of the total pore fluids. In addition to this, only a little pore water was released at the lowest speed available and a total efficiency of just 28% was achieved. In this case, fractionations may occur so 'early' samples (i.e. from lower speeds) may not be representative of the total fluid. A consideration when using this methodology is that compaction and pore size reduction may occur during centrifugation, as shown by Jones and Edwards (1993). This effect is more significant for finer textures (Gamerdinger and Kaplan, 2000). Therefore finer-textured soils would need to be tested for compaction prior to experimentation. Furthermore, a moisture content gradient also develops through the sample. As the water migrates down through the sample, the

base of the soil will be in excess of its water-holding capacity (0 kPa) during part of the centrifugation process, resulting in saturation of the sample at its base. This could cause alteration of the chemical composition of the extracted pore water, caused by a mixing process, which would homogenize the composition compared to the heterogeneous *in situ* conditions. Similar conclusions were reached by Lorenz *et al*., (1994), indicating that centrifugation yielded solution from pores of all sizes at the one time. This effect would however be much more evident at soil matric potential increasingly above FC, where preferential flow conditions and gravitational water prevail with respect to capillary water, and for single extractions. In fact, as this method is destructive and produces compaction of the soil sample, capillary conditions are most likely to be established as the extraction would proceed to later fractions, due to the reduction of the total nominal porosity.

A squeezing methodology was tested for the first time on soils. The rate of pore water collected shows that sample texture and organic matter content are important variables to consider prior to extraction. The release of water followed a linear function with very low yields for a sandy soil at FC. In these cases exceeding FC would be advisable to improve the release of pore water. Conversely, due to the higher range of pressures exerted compared to Rhizon samplers and centrifugation, a greater amount of the total available water was generally extracted. Efficiencies of 67% and 68% were observed for a clayey and a sandy silt with high organic matter respectively. The principal constraint of this methodology is the time involved. Although rapid extractions at maximum pressure are possible, the objectives of this project require a 'multiple-step at quasi-equilibrium' protocol. In this case a much longer duration, compared to centrifugation and Rhizon samplers, is required for a complete test. The duration of the extraction constitutes a major limitation, especially when organic matter is a key component of the

soil studied. Decomposition of OM and anaerobism can lead to massive variations in chemical composition and speciation. Careful consideration should therefore be made in those circumstances. For this reason, two temperatures (5°C and 15°C) will be introduced for all subsequent work in order to evaluate the extent of bacterial activity, organic decomposition and their consequences on solute composition, during pore water extractions.

4. Chemical composition, speciation and availability of trace metals in fractionated pore waters

4.1. Introduction

Knowledge of a soil's composition in terms of total elemental content is usually not very useful when it comes to understanding the processes and dynamics of element availability and cycling. Whether an element is present naturally in the soil or has been introduced by pollution, it is usually more useful to estimate the 'availability' of the element, since it is this property that can be related to mobility and uptake by plants (McBride, 1994). A good estimation of 'availability' can be achieved by measuring the concentration of the element in soil pore water. A complete chemical analysis of soil pore water represents a powerful diagnostic tool for the interpretation of many soil chemical phenomena relating to soil fertility, mineralogy, and environmental fate (Wolt, 1994), particularly when combined with models of chemical speciation to derive free ion activities.

This chapter presents the results of chemical analysis of soil pore water samples that were isolated using the three different extraction methods described in Chapter 3, and discusses the variability observed between those samples. Centrifugation and squeezing were applied in progressive steps of increasing extraction pressure, in order to extract fluid from a wider range of pore size (see sections 2.3.2, 3.3 and 3.4). The term 'fractionated samples' will be used in this chapter, and thereafter, to describe those soil pore water samples obtained by using centrifugation and squeezing in multiple steps. Rhizon samplers were also used employing a single extraction pressure, for comparison with the 'fractionated' samples derived by the other two methods.

4.2. Trace elements in soil pore water

Solute concentrations in natural waters are governed by a variety of chemical, biological and physical processes, giving rise to a wide range of compositions. The solutes found in naturally occurring water, usually present in the form of ions, can be broadly categorised as major components (i.e., present at large concentrations), and minor or trace components (i.e. at micromolar to nanomolar concentrations) (Stumm and Morgan, 1996).

Early studies in the 20th century regarding soil pore water composition were especially concerned with the major constituents (or nutrients), plant growth response and the effects of agricultural management on soil nutrient status (Cameron, 1911; Burgess, 1922). Interest in trace element solubility arose later, especially when improved analytical techniques enabled the measurement of the very low concentrations at which these elements are present in pore water. In particular, the role of these elements as essential micronutrient began to be clear from the 1950s - 1960s, when deficiencies and toxicities for some of the trace elements were found in grazing animals (e.g., Britain and New Zealand, see Thornton, 1983).

4.2.1. Speciation and toxicity

Attention was soon focused on the various forms that these components can assume in the soil-water system. Morrison *et al*., (1989) pointed out that toxicity of metals is related to the form in which they exist in the aqueous phase. This is because the interaction of metals with intracellular compartments is highly dependent on chemical speciation. Some species may be able to bind chemically with extracellular proteins and other biological molecules, some may adsorb onto cell walls, and others may diffuse through cell membranes. Consequently, toxicity is more related to the concentration of metals present as a particular species, than it is to the total metal concentration in pore water. Examples showing that metal speciation is important to metal toxicity include studies of arsenic (As), copper (Cu),

selenium (Se), and chromium (Cr). Whilst ionic copper (Cu^{2+}) and $CuCl_2^o$ are highly toxic, $CuCO_3$ and Cu-EDTA have low toxicity (Morrison *et al*., 1989). Toxicity tests show that As(III) is about 50 times more toxic than As(V). Trivalent chromium is much less toxic (excess of Cr(III) could be toxic to animals and humans) than hexavalent chromium, probably because Cr(III) is virtually insoluble (immobile) in neutral to alkaline conditions. The smaller molecular size of Cr(VI), and the chemical structure of chromate which is similar to sulphate, may lead to toxicity via special channel that exist in biomembranes for sulphate transport.

4.2.2. Factors controlling trace element speciation in pore water

Trace elements concentration may vary considerably in soils and therefore in pore water for a variety of reasons. As discussed in Chapter 1, trace elements occur naturally in rock and soils but since the start of the 19th century increasingly higher quantities of trace metals have been released into the environment by anthropogenic activities (Ross, 1996). Mobility and/or solubility of trace elements in pore water are controlled by a range of environmental factors including:

- soil pH,
- redox potential,
- adsorption and exchange capacities of soils,
- capacity for organic chelation,
- soil hydrology,
- microbial activity.

For example, soluble organic acids or mineralization of soil organic matter may form aqueous complexes with trace metals, facilitating transport to the lower mineral soil or to surface water (Perdue *et al*., 1976; Turner *et al*., 1985). Trace elements can be immobilized within the soil by adsorption, occlusion and precipitation (Gosz *et al*., 1976; Swanson and Johnson, 1980; Friedland and Johnson, 1985). The mineral soil may therefore operate either as a trace

metal sink through adsorption and precipitation reactions and/or as a trace metal source through desorption and dissolution reactions (Boggess, 1977; Driscoll *et al*., 1988; Driscoll *et al*., 1994), where solid phase composition and properties and chemical forms of metals in pore water will dictate the tendency towards one or the other direction.

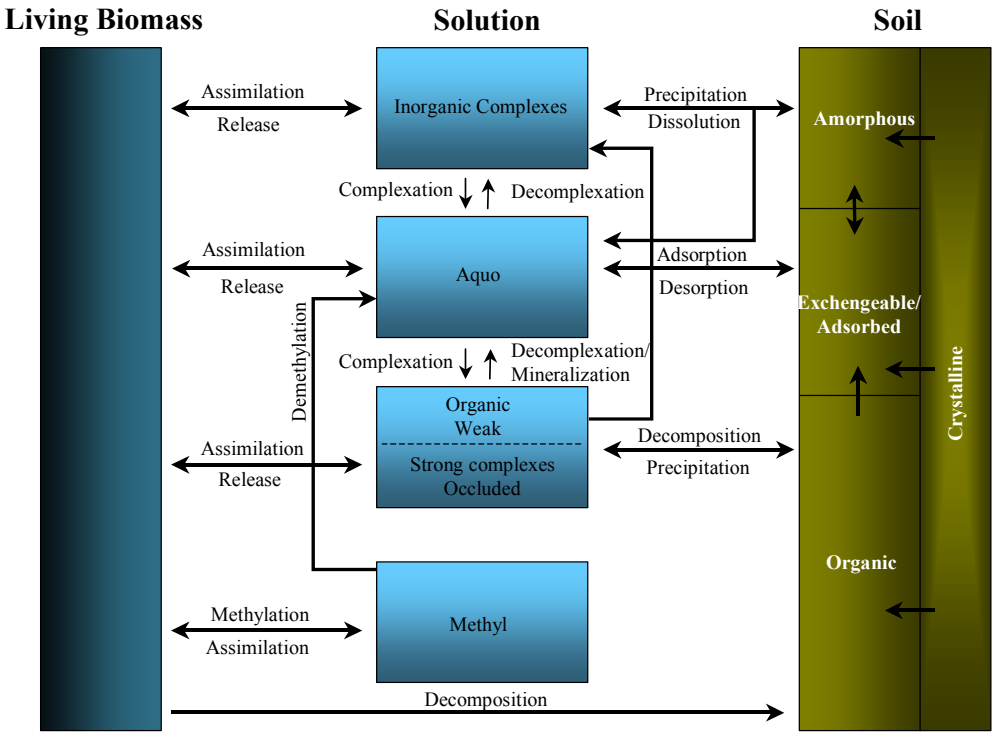


Figure 4.1. Generalized diagram of pools and transfers of trace metals in the environment.

As a consequence, trace metals can exhibit a variety of aqueous and particulate species (Fig. 4.1). Within the aqueous environment, metals can associate with a range of ligands to form complexes. These include water (aquo complexes), OH^- (hydroxo complexes), other inorganic ligands (e.g., Cl^-, SO_4^{2-}, HCO_3^-, F^-) and organic ligands. Trace metals can be mobilized/immobilized from solid phases. Solid-solution interactions of trace metals occur through adsorption/desorption reactions on organic or mineral functional groups or direct precipitation/dissolution reactions. Solid

phase metals may be associated with surface functional groups, hydroxide, carbonate or sulphide minerals (in amorphous or crystalline forms) or organic matter (Tessier *et al*., 1979). Furthermore, biota may alter the cycling of trace metals through uptake by assimilation or surface adsorption, and release by mineralization, methylation or desorption reactions. Interactions between trace metals and organisms are of particular interest in environmental chemistry because of potential nutrient deficiencies and toxicity (Simkiss and Taylor, 1989). These mechanisms (trace metal bioavailability) vary from organism to organism and metal to metal, but a detailed understanding of the interactions is only available for a few systems. In general, there are two mechanisms by which trace metals can be assimilated by organisms: (i) ionic species may form surface complexes with carrier proteins used in active transport and be transported across cellular membranes, and (ii) non-ionic species may be transported across biological membranes by passive diffusion.

In pore waters, most trace elements exist in different physico-chemical forms of various size, such as low molecular mass (LMM) ions or molecules, hydrolysis products and polymers, colloids and pseudo-colloids, or incorporated in inorganic or organic particles (Fig. 4.2). The borderline between categories is difficult to establish and transformation among categories occurs gradually. As pore waters are dynamic systems, the distribution of species exhibits spatial and temporal variations due to ongoing transformation processes. In particular, LMM species are often transformed to high molecular mass (HMM) species through one-way processes (i.e. sorption to available surfaces, complexation with available inorganic and organic ligands, polymerisation and aggregation of colloids), while desorption, dissolution, displacement and dispersion processes may mobilise LMM species from surfaces of solids.

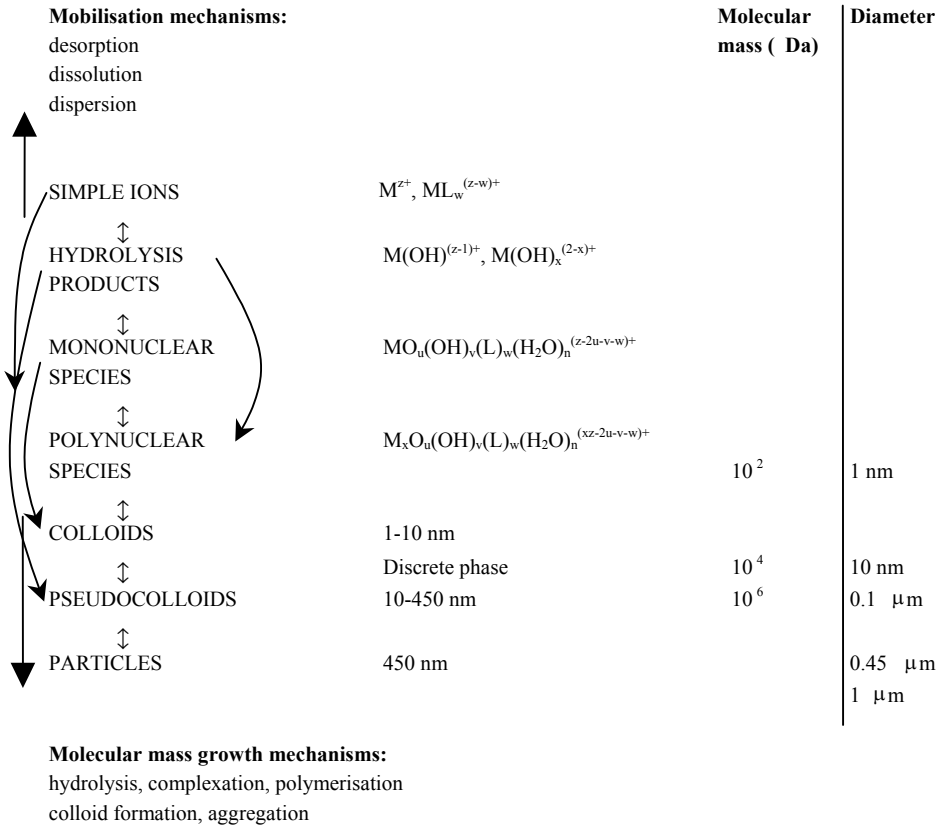


Figure 4.2. Size classes for the different physico-chemical forms of pollutants in aquatic systems. Transformation processes changing the distribution of species are indicated (from Børretzen and Salbu, 2004).

4.3. Computational models for speciation

Speciation is sometimes best evaluated by a computer model based on thermodynamic association and solubility product constants rather than by measurements (Mattigod and Sposito, 1979). Whilst analytical metal speciation is not always possible, and redox equilibrium is not achieved in all natural waters, geochemical modelling of equilibrium species distribution can be used to calculate to predict metal concentration and discern metal speciation (Zhu and Anderson, 2002). Despite the availability of over two dozen codes, only a small number of speciation programs have been used extensively by soil and environmental scientists.

Some of the reasons for the wide acceptance of the most commonly used codes by geochemists are:

1) ease and flexibility of data input,
2) availability of extensive sets of thermochemical data,
3) ease of addition and modification of code and data, and
4) the capability to model important classes of reactions such as hydrolysis, complexation, dissolution / precipitation, oxidation / reduction, ion exchange and adsorption (Mattigod 1995), as well as
5) the ability to deal with complexation by soluble humus acids.

Models evolved from simple 'functional' models, such as the early site-specific, regression-based pore water speciation models (Garrels and Christ, 1962; Truesdell and Jones, 1974) to the more complex, comprehensive models capable of representing chemical processes, including mineral formation, mineral weathering, transport and adsorption/desorption processes e.g., EQ3/6 (Wolery, 1979), SOILCHEM (Sposito and Coves, 1988), HYDRAQL (Papelis *et al*., 1988), ECOSAT (Keizer, 1991), MINTEQA2 (Allison *et al*., 1991), WHAM (Tipping, 1994), NICA-Donnan (Kinniburgh *et al*., 1996), PHREEQCi (Pankhurst and Appelo, 1999), JESS (May and Murray, 1991a, b, and c), MODELm (Huber *et al*., 2002), Biotic Ligand Model (Janssen *et al*., 2003). Although very interesting, a description of these models, their historical development and theoretical background, goes behind the scope and objectives of this project, but good sources of information can be found in the literature (Lumsdon and Evans, 1995; Suarez and Goldberg, 1994; Zhu and Anderson, 2002). Some of the characteristics for the most popular speciation models are listed in table 4.1.

Understanding of complexation reactions with inorganic ligands is well advanced because of the availability of high quality thermodynamic data and the widespread application of chemical equilibrium models (Jenne, 1979; Ball *et al*., 1980; Morel, 1983). A report about thermodynamic and kinetic databases from NEA (Nuclear Energy Agency – NEA, 1996) is available on the internet at: http://www.nea.fr/html/science/chemistry

Table 4.1. Properties of some popular speciation computer codes (modified, from Børretzen and Salbu, 2004).

	Surface complexation	Ion exchange	Activity correction	Kinetic rate laws
PHREEQC	DLM NESCM	Gaines-Thomas Gapon	Debye-Hückel Davies, B-dot	Yes
CHESS	DLM NESCM	Yes?	Davies Truncated-Davies Debye-Hückel B-dot	No
WHAM-VI	HIBM VI† SCAMP*	Donnan equilibrium	Extended Debye-Hückel, Davies	No
HYDRAQL	CCM, DLM, BSM, TLM, FLM	No	Davies	No
EQ3/6	No	No	Davies, B-dot, Pitzer	Yes
MINTEQA2	CCM, DLM, TLM	Yes?	Davies, modified Debye-Hückel	No

DLM = Diffuse Layer Model; NESCM = Non-Electrostatic Surface Complexation Model; CCM = Constant Capacitance Model; BSM = Basic Stern Model; TLM = Triple Layer Model; FLM = Four Layer Model; † Humic Ion Binding Model VI (Tipping, 1998); * (Lofts and Tipping, 1998).

However, while complexation with organic ligands is recognized as being important in trace metal speciation in freshwaters, less direct information is available. Thermodynamic data are available to describe complexation of trace metals with well-defined organic ligands (e.g. amino acids, citrate, oxalate, salicylate), but concentrations of these solutes are generally low and they are readily oxidized in the natural superficial environment (Morel, 1983; Thurman, 1985; Stevenson and Fitch, 1986). Of more importance are polycarboxyllic humic and fulvic acids (Thurman, 1985), which are becoming increasingly characterized with respect to H^+ and metal-binding reactions.

4.3.1. Humic binding and choice of speciation model

For the purposes of this study, the incorporation of humic substances into speciation was of primary importance, although this represents a major challenge for computer models due to the complex nature of these materials.

Most of the humic material in soil occurs in insoluble forms. The way in which humic substances are bound include the following (Stevenson, 1987):

1) as insoluble macromolecular complexes,
2) as macromolecular complexes bound together by di- and trivalent cations, and
3) in combination with clay minerals, such as through bridging by polyvalent cations (clay-mineral-humus), hydrogen bonding, van der Waal's forces, and other ways (see Greenland, 1971; Theng, 1979).

The ability of humic substances to form stable complexes with polyvalent cations facilitates the mobilization, transport, segregation, and deposition of trace metals in soil. Generally, humic substances are polyelectrolyte macromolecules of unknown structure, containing a range of organic functional groups. Complexation between humus and metals is mainly due to the high content of oxygen-containing functional groups, including COOH, phenolic-alcoholic, and enolic-OH, as well as C=O structures of various type and possibly amino groups. For this reason, organic macromolecules such as proteins, nucleic acids, polysaccharides, as well as synthetic polymers and humic substances, are also defined as heterogeneous multisite ligands. These macromolecules can undergo substantial changes in conformation, thereby allowing favourable binding site geometries to occur. Furthermore, the formation of complexes, in which the cation interacts with more than one polymer molecule, allows poly-dentate linkages (high denticity) to be achieved, with metals forming usually bidentate or up to tetra-coordinated complexes (Pomogailo and Wöhrle, 1996). Another major difference between organic and inorganic ligands is the existance of macromolecular electrostatic effects in the former. Organic macromolecules

develop surface charge giving rise to electrostatic interactions which influence the binding of protons and metals to each functional group (Marinsky and Ephraim, 1986).

4.3.1.1. WHAM

One of the current models developed to describe metal-binding behaviour of humic substances, is the model WHAM-VI (Windermere Humic Aqueous Model - Tipping, 1998), a speciation code specifically designed to take into account interactions with humic matter. This model was used throughout this study.

WHAM-VI is an example of '*electrostatic discrete functional group models*' (Lumsdon and Evans, 1995). In this model humic compounds are represented by hypothetical size-homogeneous, rigid, molecules, which carry proton-dissociating groups that can bind metal ions either singly or as bidentate pairs. In models of this kind the free energy of ion association is partitioned into 'chemical' and 'electrostatic' components. In addition, the 'chemical' binding energy is allowed to vary in a systematic way to allow for heterogeneity of binding site and complex configuration (Young, pers. comm.). Thus, the interactions are described in terms of intrinsic equilibrium constant and electrostatic terms. The former refer to the situation where the humic substances have zero electrical charge. The latter take into account the influence on binding of the variable humic charge; binding strength is enhanced when the metal species and the humic molecules carry opposite charges, and diminished when the charges have the same sign. As a result, the effects of variable pore water ionic strength and pH on the apparent surface acidity constants (changes in pK values, polyelectrolyte effects) are accounted for by the incorporation of an electrostatic term in the equilibrium constants, which is related to the intrinsic equilibrium constant by (Tipping *et al*., 1990):

$$K = K_{\text{int}} e^{2wzZ} \tag{4.1}$$

where e^{2wzZ} is the electrostatic term, with w the electrostatic interaction factor (depending upon ionic strength), z is the charge on the combining ion in question, and Z is the humic charge.

The proton binding groups of the humic substances are heterogeneous, having a range of intrinsic pK values. Two types of acid group are distinguished, denoted as types 'A' and 'B'. Within each type there are four different group, present in equal amounts, the pKa of which are described in terms of a median value, pK_A or pK_B, and a spreading factor ΔpK_A or ΔpK_B, that defines the range of the values.

The charge developed on the humic surface is balanced by ions adsorbed in a diffuse layer. As the net charge on the humic surface is usually negative the charge-balancing ions are usually cations. This has been incorporated by assuming a Donnan equilibrium (the Donnan law defines the volume distribution of ions on either side of a semi-permeable membrane that permits all but one ionic species to diffuse across it; if the non-diffusive ion is anionic, the Donnan model becomes analogous to a soil-water system where the net negative charge is confined to the soil surface and all other ions freely move from the surface to bulk solution – Schofield, 1947; Arnold, 1978; Talibudeen, 1981) where the following relationship applies:

$$\left(\frac{\{Me_1^{m+}\}_D}{\{Me_1^{m+}\}_S} \right)^{1/m} = \left(\frac{\{Me_1^{n+}\}_D}{\{Me_1^{n+}\}_S} \right)^{1/n} \tag{4.2}$$

where m and n are the charges on different cations (Me) in the diffuse layer (D) and the bulk solution (S). At equilibrium the above constraint conditions are met so that the sum of charges of the cations in the diffuse layer balances the charge developed on the surface. One importante feature of the latest version of WHAM is the inclusion of 'very strong' tri-dentate binding sites. Intrinsic bidentate association constants are simply the product of two

monodentate constants. However, in Model VI, there is provision for a small number of very strong binding sites where the product of monodentate constants is further multiplied by an addition factor.

For more details of the algorithmic basis of the model, see Tipping *et al.*, 1990, Tipping and Hurley, 1992, and Tipping, 1994.

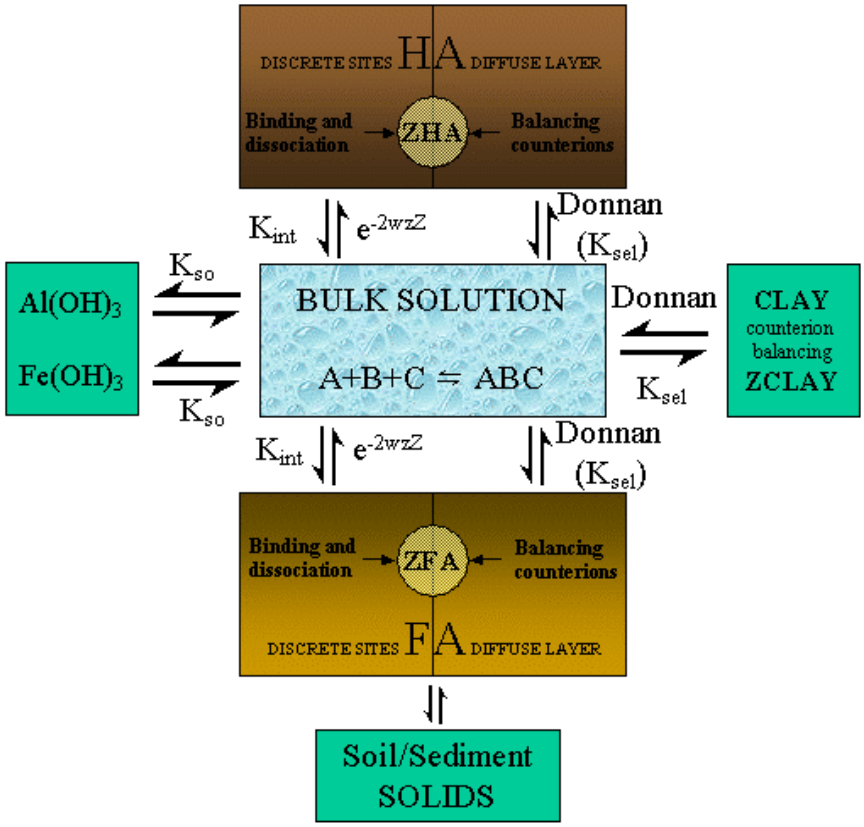


Figure 4.3. Functional relationships in WHAM; FA = fulvic acid, HA = humic acid; species in the bulk solution are in equilibrium with fulvic and humic discrete sites, and also with counterion species in diffuse layers (modified, from Tipping, 1994).

In summary, Model VI (i.e. the latest version of WHAM) takes into account both specific and non-localised (diffuse-layer) binding. The model considers HA and FA to be homogeneous materials with molecular dimensions corresponding to the average mass of real materials (Fig. 4.3). Type A sites correspond approximately to the COOH content of the humic (or fulvic) material and type B sites correspond to weaker acid moieties, e.g.

phenolic-OH. There are twice as many A sites as B sites. Part of the code constituting WHAM was also incorporated into PHREEQE under the CHEMVAL2 study (Warwick *et al.*, 1994), and by Crawford (1996) to constitute a new code, PHREEQEV. Close agreement between the PHREEQEV and WHAM predictions was achieved.

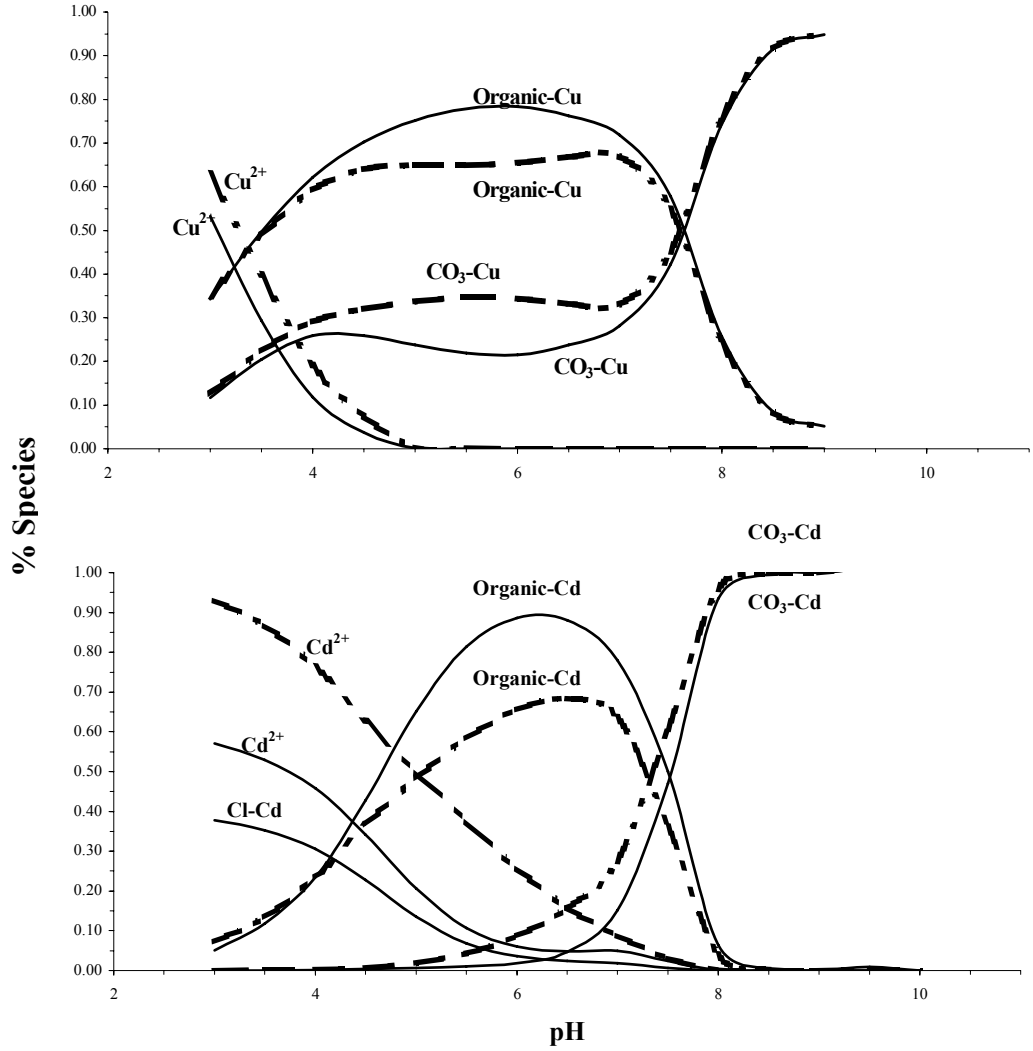


Figure 4.4. Simulation of Cu and Cd speciation using WHAM-VI; input variables: T = 25°C; Cu = 150 µg L^{-1}; Cd = 15 µg L^{-1}; pH (3-10); pCO_2 = 3.5 x 10^{-4} atm; DOC = 20 mg L^{-1}; background electrolyte 1 = 0.001 M $Ca(NO_3)_3$ (broken line), background electrolyte 2 = 0.01 M KCl (solid line).

Fig. 4.4 shows a typical output of WHAM-VI. This simple simulation was carried out on two metals (Cu and Cd) varying pH and background electrolyte, but fixing temperature, pCO_2 and the amount of DOC available for humic and fulvic complexation.

WHAM-VI has been used with success in many studies as the binding model and has been able to deal with a wide range of natural conditions, such as variable pH, competing cations, competing ligands and over a range of total metal concentration (Tipping, 2002). Good results have been obtained with soil pore waters and freshwaters containing high concentration of DOM, for which the 'active' humic matter concentration corresponds to 60-70% of the total DOM.

4.3.1.2. Some limitations in modelling with WHAM

A problem in the application of WHAM is to knowing how to represent the humic substances from measured values of DOC. There is no satisfactory way of determining the proportion of humic substances *per se*; generally, only information on organic carbon contents (DOC) is available. Therefore some assumption has to be made to estimate 'active' (in the sense of ion binding) humic and fulvic acid concentrations. In a recent work, Weng *et al*., (2002) performed model calculations by WHAM model VI, assuming two separate compositions of DOM: (i) 30% of DOM as humic acid, 30% as fulvic acid, and 40% as inert; (ii) 65% of DOM as fulvic acid and 35% as inert. Their results showed that the two assumptions for the DOM composition have generally minor effects on the predictions of metal complexation with DOM by model VI; the predicted concentrations of free metal ions using the two models were within 1 order of magnitude difference from the measured concentrations, with the exception of Ni^{2+} in one sample and Pb^{2+} in four samples. Therefore, any of these assumptions may be reliable, in the sense that results will not be highly dependent upon it, thus constituting a robust model. For this study, the first assumption, e.g., 30% HA, 30% FA and 40%

inert, was chosen. In addition, it has to be assumed that humic substances in natural samples interact with cations in the same way as their isolated counterparts. Generally, the maximum concentration of organic matter is approximately twice the DOC concentration, since humic matter is about 50% carbon by weight. Therefore, the concentration of active humic matter can only be less than or equal to twice the DOC concentration (Tipping, 2002). In practice a smaller value is usually assumed to allow for the presence of 'inert' DOC.

Another limitation of the model is due to the fact that WHAM is designed to be used for the simulation of surface water only, therefore it cannot simulate precipitation and dissolution of solids and oxidation-reduction (redox) reactions. Hence, these aspects need to be approached by classical thermodynamic calculations or by means of a different model. For this study, PHREEQCi was used as an alternative code.

4.4. Redox status - Electron Activity

Additional information for predicting and defining the behaviour of multivalent elements can be gained by the estimation of the redox potential (Eh), which represents a function of the standard potential of the reduction half-reaction and the activities of participating species through the Nernst equation. This is a numerical index of the intensity of oxidising or reducing conditions within a system, where positive potentials indicate that the system is relatively oxidising, and negative potentials indicate that it is relatively reducing. The redox status of soil pore water can also be described as a function of the apparent electron activity ($pe = -\log A_{e^-}$), which expresses soil oxidizability just as the aqueous proton is used to describe the acid–base status of the soil (Sillen, 1967). The relation between pe and Eh can be written as

$$pe = \frac{F}{2.303RT} Eh \qquad (4.3)$$

where F is the Faraday's constant (96.483 kJ V^{-1} mol^{-1}), R is the gas constant (8.314 J K^{-1} mol^{-1}), T is absolute temperature and 2.303 is the conversion from natural to base 10 logarithms (pe=5039.3Eh/T).

Unfortunately, it is recognised that soils are typically not 'well-poised' with respect to redox potential – that is, the redox behaviour of soil systems is not fixed by any one redox couple. Each redox pair will define a pe (or Eh), but their values may not be the same. If the system is at chemical equilibrium these values might be the same, but if the species involved are not in equilibrium with each other (commonly the case in natural systems), the value will be different. Therefore one can only talk about the pe (Eh) defined by a particular couple in the pore water, whereas it is misleading to attribute that value to the pore water as a whole without careful justification of what is implied (Drever, 1982). Furthermore, measured electrode potentials reflect a non-equilibrium condition along a continuum of redox potentials that approach a steady state only under strongly reducing conditions. These static anaerobic conditions are infrequently manifested in soils, surface or ground water since these systems are never totally isolated from the atmosphere. A further complication arises from the low concentrations of redox species existing in most natural aqueous solutions.

In addition to pe (redox level or redox intensity), *redox buffering* (or *redox capacity*) is another important concept to account for. A system is buffered (or 'poised') with respect to redox processes if oxidisable or reducible compounds are present that prevent a significant change in pe in response to addition of small amounts of strong oxidising or reducing agents.

In aerobic soils, O_2 is the major electron acceptor and acts to buffer electron activity. In the face of limited O_2 in the soil, microbes will use successively less effective electron acceptors as sources of reducing power.

As soil become progressively anaerobic, pH tends to stabilise due to the buffering effect of accumulated CO_3^{2-} and HCO_3^-.

The most important chemical elements affected by soil redox reactions are C, N, O, S, Mn and Fe (Sposito, 1989). In contaminated soils, this list would be extended to include As, Se, Cr, Hg and Pb. If a soil is behaving effectively like a closed system (e.g., a flooded soil under stagnant ponding) and abundant sources of carbon and energy are available to support microbially mediated catalysis, there is a well-defined sequence of reduction of the inorganic elements through the principal six reduction half-reactions (Table 4.2).

Table 4.2. Order of utilization of principal electron acceptors in soils, Eh at pH 7 (from Bohn *et al.*, 1985 - modified); pe calculated using equation (4.3).

Reaction	E_{h7}	pe 5°C	pe 15°C
O_2 disappearance $\frac{1}{2} O_2 + 2e^- + 2H^+ = H_2O$	0.82	14.86	14.34
NO_3^- disappearance $NO_3^- + 2e^- + 2H^+ = NO_2^- + H_2O$	0.54	9.79	9.45
Mn^{2+} formation $MnO_2 + 2e^- + 4H^+ = Mn^{2+} + H_2O$	0.4	7.25	7.00
Fe^{2+} formation $FeOOH + e^- + 3H^+ = Fe^{2+} + 2H_2O$	0.17	3.08	2.97
HS^- formation $SO_4^{2-} + 6e^- + 9H^+ = HS^- + 4H_2O$	-0.16	-2.90	-2.80
H_2 formation $H^+ + e^- = \frac{1}{2} H_2$	-0.41	-7.43	-7.17
CH_4 formation $(CH_2O)_n = n/2\ CO_2 + n/2\ CH_4$	-	-	-

The table shows that N and Mn reductions occur before that of Fe. In fact, Fe reduction only starts when both N and Mn have been completely reduced, which makes using Fe concentrations not always reliable and/or easy to assess and calculate redox potential. In addidion, Fe ions are not always easily detectable by some analytical techniques; in the case of ICP-MS analyses, used throughout this study, Fe ions have low detection limits and are often 'obscured' by Ca interferences. For these reasons, redox

interpretations were mostly based on Mn and N observation rather than Fe in this study. In particular, Mn was also used for redox potential calculations and to assess redox conditions of the extraction conditions.

4.4.1. Role of Manganese

In the context of redox reactions, manganese oxides play a unique role in aerobic soils as highly adsorptive colloidal materials interacting with both soil minerals and organic fractions. Mineralogically complex, these oxides are practically universal above pH 5 as mineral coatings and nodules on or near well-aerated surfaces (Bartlett, 1986). Because they coat surfaces, they exert a chemical influence far out of proportion to their total concentration (Jenne, 1977). Mn oxides have extremely high surface areas and cation adsorption capacities and appear to act as strong scavenging agents for heavy metals (Chao, 1972). Surface charge on Mn oxides is pH dependent, with negative charges increasing markedly as pH increases above 5 (Possett and Anderson, 1968).

In oxidised forms, Mn is resistant to leaching, but once reduced to the divalent ion, it can be leached quickly from the matrix. McBride (1982) showed in Electron Spin Resonance (ESR) studies that at soil pH greater than 5 or 6, Mn^{2+} is held by soil organic matter in inner sphere (chelate) complexes, but that bonding to more acid organic matter is by outer sphere (electrostatic) forces.

Reduction of Mn oxides has dual effects on soil cation solubility. Not only does the oxide adsorption surface disappear, but the newly formed Mn^{2+} ion enters into sorption competition with other cations. Activities and susceptibility to leaching of Ca, Mg, and adsorbed heavy metals increases as Mn reduces (Bartlett, 1986).

Jenne (1977) proposed that the presence of hydrous oxides of Mn and Fe provides the principal control on the fixation of Co, Ni, Cu and Zn in soils and freshwater sediments. By selectively reducing a landfill soil, Suarez and Langmuir (1976) showed that Mn-rich oxides had at least ten times the heavy

metal content of Fe-rich oxides, reflecting their greater potential for coprecipitation with other trace metals. McKenzie (1978) found that the addition of MnO_2 to Pb-contaminated soil lowered the uptake of Pb, Co, and to a lesser extent, Ni, by subterranean clover. The availabilities were related to the distribution of these elements between Mn and Fe oxides in the soils. According to Loganathan *et al*., (1977), specific adsorption of Co and Zn by MnO_2, compared to Ca, was related to hydroxylation of the metal ions as pH was increased above 6. The oxidation of some elements (i.e. V, Se, Hg, Mo, and Cu) by Mn oxides is thermodynamically feasible and the study of the redox behaviour of these elements in soil is an area which merits research, especially in terms of adsorption and toxicity. Adsorption of Co(II) onto MnO_2 resulted in its oxidation to Co(III), accompanied by the reduction of Mn(IV) (Hem, 1978; Murray and Dillard, 1979). Toxic As(III) (arsenite) was shown by Oscarson *et al*., (1981), to be oxidised to the less toxic As(V) (arsenate) form by Mn oxides in sediments. Bartlett (1986) reports studies on Cr and Pt redox reactions as affected by soil Mn oxides where it was concluded that Cr behaviour could be used as a qualitative model for Pt oxidation in soils, which was shown to be converted to the mobile anion form, similarly to chromate, if oxidised by soil Mn oxides.

4.5. Objectives

In the following sections, an experiment is described and performed in order to extract soil pore water from different classes of pores, using three methods of extraction: Rhizon samplers, centrifugation and pressure filtering (squeezing), each one based on a different physical principle (see Chapter 3). Incremental pressure steps were performed during extractions for centrifugation and squeezing. The experiment aimed at clarifying the existence of difference in chemistry for the pore waters extracted and discusses genuine differences caused by variation of master pore water

variables, such as pH, redox and speciation as distinct from artefacts arising from the methods employed.

4.6. Materials and methods

4.6.1. Soil sampling and pre-treatment

The soil used in this experiment was from Stoke Bardolph. Its sampling and pre-treatments are described in section 2.5.1.

4.6.2. Pore water extraction

Samples of soil pore water were extracted from the incubated soil (FC moisture content, 5° C and 15° C) using three different techniques (see section 3.4):

1) rhizon samplers (Soil Moisture Samplers - SMS);
2) drainage centrifugation;
3) 'pressure filtering' (squeezing).

4.6.2.1. Rhizon samplers

Rhizon SMS were used for pore water sampling following the procedure described in section 3.4.2.4 (Knight *et al*., 1998; Tye *et al*., 2003).

4.6.2.2. Centrifugation

The centrifuge drainage technique as described in section 3.4.3.3 (Edmund and Bath, 1976; Gooddy *et al*., 1995) was employed using a Beckman J2-21 high-speed refrigerated centrifuge, with the modification of fractionating the soil pore water by incremental increases in the centrifugation speed (Tyler, 2000). Samples were centrifuged for 1 hour, as suggested also by Grieve (1996) and Pérez *et al*., (2002), at two different temperatures, 5°C and 15°C, in 5 consecutive steps, at Relative Centrifugal Field (RCF × *g*) values of: 110, 439, 1345, 2744 and 5075. The resulting driving pressures at the midpoint

during each fraction step centrifugation, calculated using the equation (3.5), were: 18, 70, 214, 438 and 809 kPa respectively.

The five water fractions extracted were collected separately, weighed and then syringe ultra filtered through a 0.45 µm Nylon Acrodisc Syringe Filter (Pall-Gelman - HPLC certified) and separated into two aliquots, one of which was acidified to 1% HNO_3 v/v into 15 ml Nalgene bottles for elemental analysis by ICP-AES or ICP-MS. The fractions of three centrifuge tubes were combined to have enough water for the analysis and the whole run repeated twice to have adequate number of replicates (4) for each sample. When the test was completed, the soil contained in the tubes was weighed and oven dried at 105°C for determination of moisture content.

4.6.2.3. Pressure filtering (Mechanical squeezing)

The 'pressure filtering' technique (or soil mechanical squeezing) was undertaken at the British Geological Survey (Keyworth, Nottingham, UK) as described in section 3.4.4. A protocol of incremental pressures to apply to the soil samples was decided with steps at: 200, 500, 1000, 1500, 3000, 9000 and ca. 50000 kPa. When the soil sample stopped releasing pore water at a specific pressure (< 1 ml collected in 18-24 h), the syringe was removed and the sample filtered as soon as collected through a 0.45 µm Nylon Acrodisc Syringe Filter. The samples were poured into 30 ml Nalgene bottles and treated as for previously described extractions. Further fractions of sample were collected, using a new syringe assembly, until no further pore water could be obtained (Cave *et al.*, 1998). When the test was completed, the test soil was weighed and oven dried at 105°C for density and determination of moisture content.

4.6.3. Chemical analysis

All chemical analyses (pH, major cations and anions, trace elements and total organic and inorganic carbon) were carried out as described in section 3.4.6.

4.6.4. Redox potential calculations

Redox calculations were based on the reduction half-reaction:

$$\frac{1}{2}MnO_2(s) + 2H^+(aq) + e^-(aq) = \frac{1}{2}Mn^{2+}(aq) + H_2O(l) \qquad (4.4)$$

where $Mn^{2+}_{(aq)}$ represents the free ion concentration, and equation (4.3). In this way it was possible to calculate the corresponding Eh values for a given activity of Mn^{2+}, giving an estimate of the redox conditions of the system. In reduction half-reactions, such as equation (4.4), the reduction of the proton (reaction on the right) is defined to have log K = 0. In this way, the reduction half-reaction can be used to predict the ranges of pe (Eh) and pH over which one redox species or another predominates (Sposito, 1989). Assuming both the solid-phase and liquid water activities equal to 1.0 (it is customary to), Eh can be written as:

$$Eh = 2.303\frac{(\log k_{eq} - \frac{1}{2}\log(Mn^{2+}) - 2pH)}{F}RT \qquad (4.5)$$

where (Mn^{2+}) is the activity of $Mn^{2+}_{(aq)}$ in pore water (as calculated by WHAM-VI). The equilibrium constant log k_{eq} will depend on the temperature and is calculated according to the van't Hoff equation:

$$k_{eq1} = k_{eq2}\exp\left[\frac{\Delta H_r^o}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right] \qquad (4.6)$$

where k_{eq1} represents the initial or known equilibrium constant (usually at 25°C), T is the temperature in Kelvin (K), ΔH_r° is the standard enthalpy of reaction (J mol^{-1}), R the gas constant (8.31447 J K^{-1} mol^{-1}) and k_{eq2} the equilibrium constant at the required temperature (Atkins and de Paula, 2001).

ΔH_r° and k_{eq1} were calculated at standard conditions (298.15K) using thermodynamic properties of pure substances and aqueous solutes[5], and were respectively:

$\Delta H_r^\circ = (-)136190$ J mol^{-1}

$k_{298} = k_{eq1} = 5.02 \times 10^{20}$ $(\ln k_{eq1} = 47.7)$

As a result, k_{eq2} for 5°C and 15°C will be:

$k_{278} = 9.33 \times 10^{18}$ $(\ln k_{278} = 43.7)$

$k_{288} = 7.22 \times 10^{19}$ $(\ln k_{288} = 45.7)$

4.6.5. Chemical speciation

Metals in the soil pore waters were speciated using the model WHAM-VI (Tipping, 1998). Input files included total pore water concentrations for Na, Mg, Al, K, Ca, Cr(III), Mn, Co, Ni, Cu, Zn, Sr, Cd, Ba, Pb, Cl, NO_3, SO_4, PO_4, AsO_4, temperature (5°C and 15°C) and pore water pH. Fe(III) activity was included as a variable, and calculated from (Loft, S., pers. comm.):

$$\log_{10}\{Fe^{3+}\} = \log_{10} K_{SO} - 3pH \qquad (4.7)$$

where

$$\log_{10} K_{SO} = \log_{10} K_{SO}^{0} + \left[0.219\Delta H^\circ \left(\frac{1}{298}\right) - \left(\frac{1}{T}\right)\right],$$

[5] http://www.psigate.ac.uk/newsite/reference/chemdata/3.html

$\log_{10} K^{0}_{SO} = 2.7$ at 298K

ΔH^{o}, the standard reaction enthalpy, has a value of –104600 J mol^{-1}

This is particularly important in WHAM-VI because Fe^{3+} is a major competitor for the small number of very strong binding sites on HA and FA hypothesised in Tipping's Model VI.

Measured DOC was converted to concentrations of HA and FA, following the approach suggested by Weng *et al*., (2002): 30% of DOC as humic acid, 30% as fulvic acid, and 40% as inert, where FA and HA both contain 50% C. The model allows the simulation of the carbonate system in equilibrium with atmospheric CO_2 (open system) or decoupled from the atmosphere (closed system). For the soil studied, dissolved inorganic carbon (DIC) was included as the WHAM master variable 'CO_3' to account for carbonate alkalinity. All free ion and complex concentrations and activities are included in the output of the model.

Pore waters were also modelled using PHREEQCi version 2.8.0.0 (Parkhust and Appelo, 1999), a program based on equilibrium chemistry of aqueous solutions, written in the C programming language and available as freeware from the internet[6]. PHREEQCi is based on an ion-association aqueous model but also includes the capability to model kinetic reactions with rate equations user-specified. The code incorporates a diffuse double-layer model (Dzombak and Morel, 1990), a model with an explicitly calculated diffuse layer (Borkovec and Westall, 1983) and a non-electrostatic model (Davis and Kent, 1990) for modelling surface-complexation reactions. Surface complexation constants from Dzombak and Morel (1990) are included in the default databases for the program. Several databases are available within the code: *phreeqc.dat* and *wateq4f.dat*, taken from Dzombak and Morel (1990), *minteq.dat* taken from MINTEQA2 (Allison *et al*., 1990), and *llnl.dat*, taken from the Geochemist Workbench (Bethke, 1996). Ion-exchange

reactions are modelled with the Gaines-Thomas convention and equilibrium constants derived from Appelo and Postma (1994) are included in *phreeqc.dat* and *wateq4f.dat*.

PHREEQCi was used as a speciation program to calculate saturation indices for potential solid phases and the distribution of aqueous species for elements not supported by the WHAM model. Analytical data for mole balances were defined for any valence state or combination of valence states for an element. Distribution of redox elements among their valence states, based on a specified Eh or any redox couple for which data were available or calculated, were also determined.

4.7. Results and discussion

4.7.1. Overview of the geochemical dataset

Statistical summaries of the data generated are given in Tables 4.3 and 4.4 and Fig. 4.5 where, for simplicity, elements are organised in increasing order of mean value. Values below the lower limit of detection were assigned a value of one half of the detection limit, as recommended by Albert and Horowitz (1995), prior to statistical treatment of the datasets.

As expected from the nature of the soil studied, some trace element are present in unusually high concentrations (Ni, Zn, Mo, As, Mn Cu and Cd) compared to 'typical' values in soils and soil pore waters (values reported in Table 4.3 and 4.4 taken from Table 1.1.), whereas some of the normally abundant or major elements in soil were found to be present in very small concentrations (Fe) in the pore water. The most variable measurements were Br, NO_2, Pb, DIC, Mn and to a lesser extent Fe, V, Mo (Fig. 4.5 and Tables 4.3 and 4.4).

[6] http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/ or http://www.geo.vu.nl/users/posv/phreeqc.html

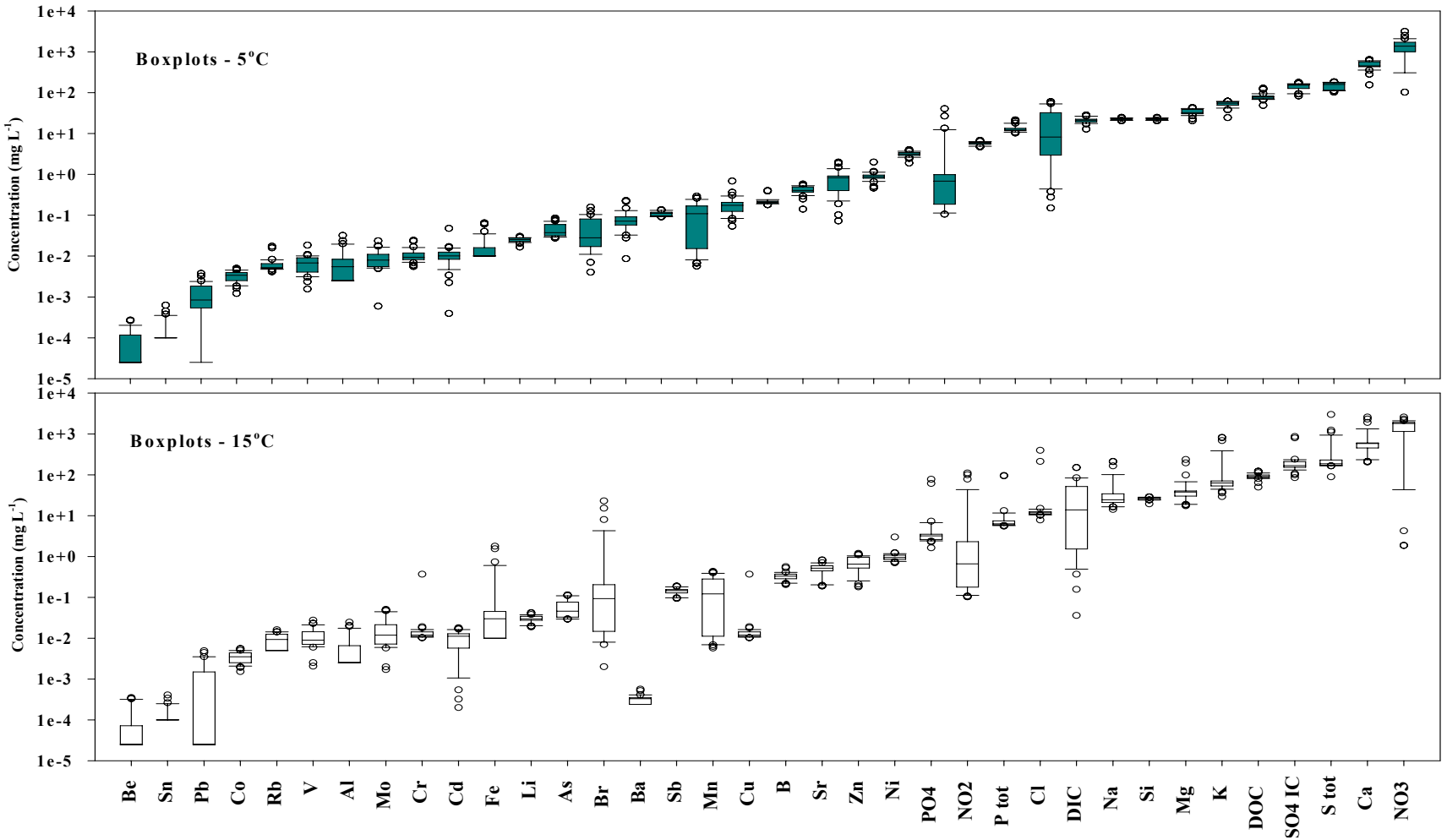


Figure 4.5. Comparison of solute concentrations at 5°C and 15°C between the three extraction methods (see also Table 4.3 and 4.4); data sorted by increasing mean. The distance between the top and bottom sides of the box represent the interquartile range, the mid-bar is the median. Whiskers extend to the outermost data point, or 10th and 90th percentile when they exist. Outlier values (o) are defined as values less than 10th and beyond 90th percentile.

Table 4.3. Descriptive statistics of the dataset at 5°C; data ordered by increasing mean; in brackets some mean typical pore water concentrations taken from Table 1.1; all concentrations in mg L^{-1}.

	Mean	St. Error	Median	St. Deviation	Min	Max
			5°C			
Be	7.74×10^{-5}	1.33×10^{-5}	2.50×10^{-5}	7.55×10^{-5}	2.5×10^{-5}	2.72×10^{-4}
Sn	1.55×10^{-4}	2.2×10^{-5}	1.00×10^{-4}	1.24×10^{-4}	1.0×10^{-4}	6.24×10^{-4}
Pb	0.0011 **(0.0010)**	1.7×10^{-4}	8.42×10^{-4}	9.61×10^{-4}	2.5×10^{-5}	0.0038
Co	0.0033 **(0.0047)**	1.67×10^{-4}	0.0034	9.46×10^{-4}	0.0012	0.0050
Rb	0.0063	5.1×10^{-4}	0.0052	0.0029	0.0041	0.0172
V	0.0068	5.82×10^{-4}	0.0068	0.0033	0.0016	0.0184
Al	0.0073	0.0012	0.0055	0.0071	0.0025	0.0319
Mo	0.0088 **(3.84×10^{-5})**	8.11×10^{-4}	0.0079	0.0046	5.89×10^{-4}	0.0235
Cr	0.0107 **(0.0541)**	7.51×10^{-4}	0.0093	0.0042	0.0055	0.0242
Cd	0.0110 **(0.0045)**	0.0013	0.0101	0.0076	3.91×10^{-4}	0.0473
Fe	0.0160	0.0024	0.0100	0.0139	0.0100	0.0650
Li	0.0250	5.24×10^{-4}	0.0253	0.0030	0.0166	0.0303
As	0.0447 **(7.49×10^{-4})**	0.0030	0.0374	0.0170	0.0273	0.0846
Br	0.0487	0.0073	0.0280	0.0402	0.0040	0.1570
Ba	0.0792	0.0081	0.0715	0.0457	0.0086	0.2271
Sb	0.1095	0.0023	0.1106	0.0132	0.0910	0.1353
Mn	0.1108 **(5.20×10^{-4})**	0.0151	0.1086	0.0857	0.0057	0.2924
Cu	0.1862 **(0.0635)**	0.0200	0.1746	0.1133	0.0533	0.6854
B	0.2211	0.0085	0.2100	0.0484	0.1800	0.4000
Sr	0.4153	0.0163	0.4020	0.0925	0.1397	0.5782
Zn	0.7731 **(0.0052)**	0.0788	0.8253	0.4455	0.0720	1.9869
Ni	0.8981 **(0.010)**	0.0447	0.8688	0.2531	0.4597	1.9888
PO_4	3.1286	0.0806	3.1355	0.4417	1.8803	3.9906
NO_2	3.7413	1.6135	0.7035	8.8373	0.1050	40.154
P tot	5.7527	0.0867	5.8650	0.4902	4.6600	6.7300
Cl	13.110	0.4972	12.167	2.7231	10.255	21.406
DIC	17.895	3.5408	8.2210	19.394	0.1500	59.900
Na	21.261	0.5767	21.150	3.2624	12.780	28.020
Si	22.557	0.1973	22.796	1.1162	20.290	24.640
Mg	33.633	0.9739	32.175	5.5093	20.420	42.910
K	52.949	1.4628	55.120	8.2748	24.260	61.640
DOC	79.420	2.7453	78.100	15.036	48.390	128.70
SO_4	138.54	5.1239	152.80	28.065	82.717	176.45
S tot	148.82	4.9839	158.68	28.193	102.16	184.09
Ca	473.28	18.772	451.13	106.19	154.40	641.29
NO_3	1464.5	108.57	1381.2	594.68	102.60	3114.0

Table 4.4. Descriptive statistics of the dataset at 15°C; data following the same order as on Table 4.3 (for comparison); in brackets some mean typical pore water concentrations taken from Table 1.1; all concentrations in mg L^{-1}.

	Mean	St. Error	Median	St. Deviation	Min	Max
			15°C			
Be	8.45×10^{-5}	1.91×10^{-5}	2.5×10^{-5}	1.13×10^{-4}	2.5×10^{-5}	3.51×10^{-4}
Sn	1.28×10^{-4}	1.25×10^{-5}	1.0×10^{-4}	7.39×10^{-5}	1.0×10^{-4}	4.05×10^{-4}
Pb	0.0010 **(0.0010)**	2.39×10^{-4}	2.5×10^{-5}	0.0014	2.5×10^{-5}	0.0049
Co	0.0035 **(0.0047)**	1.81×10^{-4}	0.0035	0.0011	0.0015	0.0056
Rb	0.0087	6.61×10^{-4}	0.0093	0.0039	0.0050	0.0160
V	0.0110	9.79×10^{-4}	0.0089	0.0058	0.0021	0.0274
Al	0.0058	0.0010	0.0025	0.0061	0.0025	0.0244
Mo	0.0170 **(3.84×10^{-5})**	0.0023	0.0118	0.0136	0.0017	0.0507
Cr	0.0228 **(0.0541)**	0.0101	0.0119	0.0599	0.0101	0.3667
Cd	0.0094 **(0.0045)**	8.39×10^{-4}	0.0111	0.0050	2.01×10^{-4}	0.0180
Fe	0.1542	0.0759	0.0300	0.4227	0.0100	1.7785
Li	0.0300	0.0010	0.0297	0.0059	0.0188	0.0421
As	0.0544 **(7.49×10^{-4})**	0.0045	0.0457	0.0266	0.0290	0.1139
Br	0.0989	0.0202	0.0570	0.1104	0.0020	0.4130
Ba	2.94×10^{-4}	2.21×10^{-5}	3.3×10^{-4}	1.31×10^{-4}	2.05×10^{-4}	5.65×10^{-4}
Sb	0.1422	0.0045	0.1465	0.0265	0.0936	0.1882
Mn	0.1499 **(5.20×10^{-4})**	0.0250	0.1214	0.1481	0.0057	0.4317
Cu	0.1685 **(0.0635)**	0.0113	0.1886	0.0668	0.0177	0.2982
B	0.3323	0.0143	0.3300	0.0797	0.2050	0.5650
Sr	0.5010	0.0280	0.5167	0.1654	0.1869	0.8182
Zn	0.6978 **(0.0052)**	0.0482	0.6481	0.2851	0.1782	1.1888
Ni	1.0025 **(0.010)**	0.0625	0.9470	0.3697	0.6970	2.9770
PO_4	3.2737	0.1958	3.1395	1.1079	1.6283	7.2829
NO_2	1.7824	0.6084	0.3990	3.3873	0.1030	15.745
P tot	6.7704	0.2704	6.3000	1.5055	5.4800	13.195
Cl	11.576	0.2266	11.630	1.2817	7.7880	15.060
DIC	21.966	4.6794	10.632	26.881	0.0360	84.400
Na	25.164	1.2353	24.025	6.8776	14.100	36.885
Si	26.101	0.3391	26.476	1.8883	19.325	28.720
Mg	33.741	1.4859	36.880	8.2731	17.400	47.190
K	59.317	2.1034	61.125	11.711	29.100	77.030
DOC	92.241	2.4530	91.020	14.091	49.590	121.74
SO_4	171.38	6.4854	165.73	36.687	84.705	237.94
S tot	190.40	6.0339	182.12	33.595	88.990	264.29
Ca	504.93	26.198	576.38	145.86	203.00	756.43
NO_3	1474.8	128.09	1795.6	724.58	1.8530	2574.9

Element concentrations appear to be greater following incubations at 15°C. Table 4.5 presents *p* values resulting from ANOVA of the dataset considering the effect of the temperature on the concentration variability. This effect is very significant for some elements ($p < 0.001$ - B, Br, Cr, organic and inorganic C, K, Li, Mo, Na, P tot, Rb, S tot and SO_4, Sb, Si, Sr, and V), which in turn can have considerable implications for speciation and bioavaiilability. However, the temperature seems to have no significant effect on the concentration of other elements (Al, Ba, Be, Cd, Co, Cu, Fe, Mg, Mn, Ni, NO_2 and NO_3, Pb, PO_4, Sn, and Zn), which may suggest different behaviour as a result of different chemical properties of the elements.

Table 4.5. ANOVA results and p values for datasets at 5°C and 15°C; * = p < 5% (0.05) = significant difference; ** = p < 1% (0.01) = highly significant; *** = p < 0.1% (0.001) = very high significant; NS = not significant. Where there are significant differences 5>15 denotes that concentrations at 5°C are greater that those at 15°C; 5<15 denotes that concentrations at 15°C are greater than those at 5°C.

Parameter	Temperature effect		Means	Parameter	Temperature effect		Means
	p				p		
PO_4	0.909	NS		**Cl**	0.001	**	5>15
Be	0.703	NS		**B**	<.001	***	5<15
Cu	0.608	NS		**Br**	<.001	***	5<15
NO_3	0.586	NS		**Cr**	<.001	***	5<15
Pb	0.57	NS		**DIC**	<.001	***	5<15
Ba	0.542	NS		**DOC**	<.001	***	5<15
Cd	0.474	NS		**K**	<.001	***	5<15
Co	0.439	NS		**Li**	<.001	***	5<15
Sn	0.416	NS		**Mo**	<.001	***	5<15
Al	0.324	NS		**Na**	<.001	***	5<15
Mg	0.215	NS		**P tot**	<.001	***	5<15
NO_2	0.164	NS		**Rb**	<.001	***	5<15
Zn	0.144	NS		**S tot**	<.001	***	5<15
Fe	0.117	NS		**Sb**	<.001	***	5<15
Mn	0.099	NS		**Si**	<.001	***	5<15
Ni	0.076	NS		**SO_4**	<.001	***	5<15
pH	0.037	*	5>15	**Sr**	<.001	***	5<15
As	0.029	*	5<15	**V**	<.001	***	5<15
Ca	0.019	*	5<15				

In general, the different concentrations at the two temperatures seem to suggest greater solubility of solutes at higher temperatures. In a recent work, Richards and Kump (2003) suggested that temperature affects the release of solutes from soils in two ways; first directly, by modifying surface tension, water viscosity, dissolution rate, diffusion rate and equilibrium constants of the mineral present, and second indirectly, by influencing the level of biological activity. Temperature will therefore affect both the volume of water withdrawn from a soil and its chemical composition. A temperature-induced change in surface tension and water viscosity, which in turn influences hydraulic conductivity, will change the size class of micropores that can drain and at the same time will cause variation of water residence time as well as desorption rate constant and equilibrium constants.

It is interesting to note the difference between the first samples obtained by squeezing or centrifugation and those obtained by Rhizon samplers. Table 4.6 presents *p* values resulting from ANOVA of the dataset considering the effect of the method of extraction but comparing only the first samples extracted by centrifugation and squeezing with the one extracted by Rhizon samples. Concentrations are also shown in Fig. 4.6 – 4.17. Typically soil pore water would not be withdrawn in multiple steps and would not reach the pressures used in the squeezing method. More frequently one would use a single extraction (as in the Rhizon sampler case) or a single step with centrifugation. Alternatively, samples coming from different stages of the extraction are usually bulked. The method of extraction does not affect significantly the concentrations of some elements (Br, Cd, Cl, Cu, DIC, Fe, Ni, NO_2 and NO_3, P tot and PO_4, Rb, Sb and SO_4) but appears to be significant for the rest of them. In most cases, their concentrations in pore waters taken by Rhizon samplers are smaller than those from centrifugation and squeezing (Table 4.6 - R<C<S – Ca, Co, Li, Mg, Mn, Mo, Na, S tot, Si, Sr and V; R<S<C –

B, Ba, Cr, Organic C, and K). A smaller group of elements shows concentrations in pore waters taken by squeezing smaller when compared to those taken by centrifugation and Rhizon sampler (Table 4.6 - S<R<C – Al, Pb, Sn and Zn). When we consider the methods individually, data show different degrees of variability across the 3 different methods of extraction. The variation is much greater within extracted samples by squeezing, whereas centrifugation data appear less variable. The greater variation within the squeezing data is due to the use of three different sets of apparatus, which, although set with exactly the same parameters (i.e., mass and conditions of soil, pressure and temperature), may vary in their mechanical performances (Table 4.6 and Fig 4.6 – 4.17).

Table 4.6. ANOVA results and p values for 1st samples of different extraction methods (R = Rhizon samplers, C = Centrifugation, S = Squeezing); * = p < 5% (0.05) = significant difference; ** = p < 1% (0.01) = highly significant; *** = p < 0.1% (0.001) = very highly significant; NS = not significant. Where there are significant differences, the last column on the right shows which extraction method (R, C and S) presents greater concentrations compared to the others.

Parameter	Method effect		Means	Parameter	Method effect		Means
	p		1st sample		p		1st sample
PO_4	0.728	NS		**Si**	0.004	**	R<C=S
NO_2	0.561	NS		**Sr**	0.003	**	R<C<S
Rb	0.501	NS		**Ba**	0.002	**	R<S<C
Sb	0.358	NS		**V**	0.002	**	R<C<S
Cd	0.319	NS		**Mg**	0.001	**	R<C<S
Br	0.249	NS		**Al**	<.001	***	S<R<C
SO_4	0.239	NS		**B**	<.001	***	R<S<C
Cu	0.221	NS		**Ca**	<.001	***	R<C<S
P tot	0.191	NS		**Co**	<.001	***	R<C<S
NO_3	0.123	NS		**Cr**	<.001	***	R<S<C
Ni	0.083	NS		**DOC**	<.001	***	R<S<C
DIC	0.081	NS		**K**	<.001	***	R<S<C
Fe	0.08	NS		**Mn**	<.001	***	R<C<S
Cl	0.064	NS		**Mo**	<.001	***	R<C<S
Be	0.05	*	R=C<S	**Na**	<.001	***	R<C<S
Sn	0.034	*	S<R<C	**Pb**	<.001	***	S<R<C
As	0.03	*	R=C<S	**pH**	<.001	***	R<C<S
Li	0.012	*	R<C<S	**S tot**	<.001	***	R<C<S
				Zn	<.001	***	S<R<C

Grouping the elements by their position in the periodic table, we can start to account for similar or dissimilar behaviour (Fig. 4.6 – 4.17). Alkali and alkaline earth metals decreased in concentration with progressive extractions, both using centrifugation and squeezing at both temperatures. Very similar behaviour was shown by K, Na, Li, Ba, Ca, Mg and Sr in this respect.

Transition metals, showed a similar behaviour between the two temperature datasets, but in this case some elements appeared to decrease in concentration (Pb, Al, Fe, Cd, Cu, Zn and Ni), some other seem to increase with progressive extractions (Mo, V, Co, Mn), whereas the remainder appear to have different behaviour between methods of extraction (Co, Cu, Cr).

Non-metallic elements, which include most of the anions, present contrasting behaviour. Some increased in concentration during squeezing (S, HCO_3, As, P, Br and to a lesser extent Si) but were fairly constant with progressive centrifugation. Others decreased with centrifugation (B, Cl, Si) or decreased during squeezing (NO_3).

Organic Carbon showed similar behaviour between the two temperatures. However, samples withdrawn by Rhizon samplers showed lower concentrations of DOC compared to the other two methods, sometimes presenting better agreement with centrifugation data rather than with squeezing. The pH was fairly constant during centrifugation whereas it increased in squeezed samples.

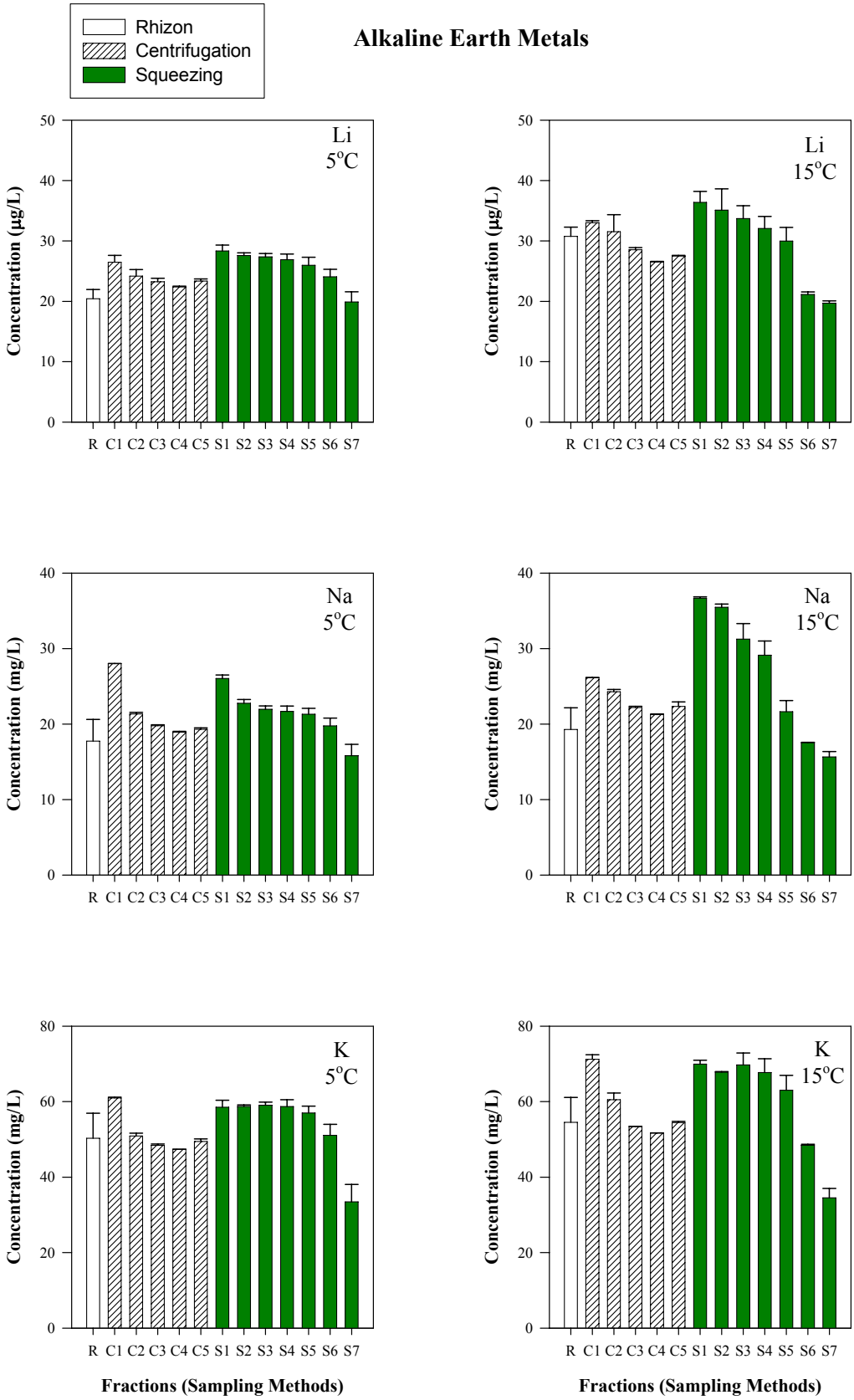


Figure 4.6. Element concentrations for pore water fractions at 5°C and 15°C for Stoke Bardolph: Alkaline Earth Metals; R = Rhizon samplers, C (1-5) = Centrifugation, S (1-7) = Squeezing; concentrations in mg L^{-1} or µg L^{-1} as stated.

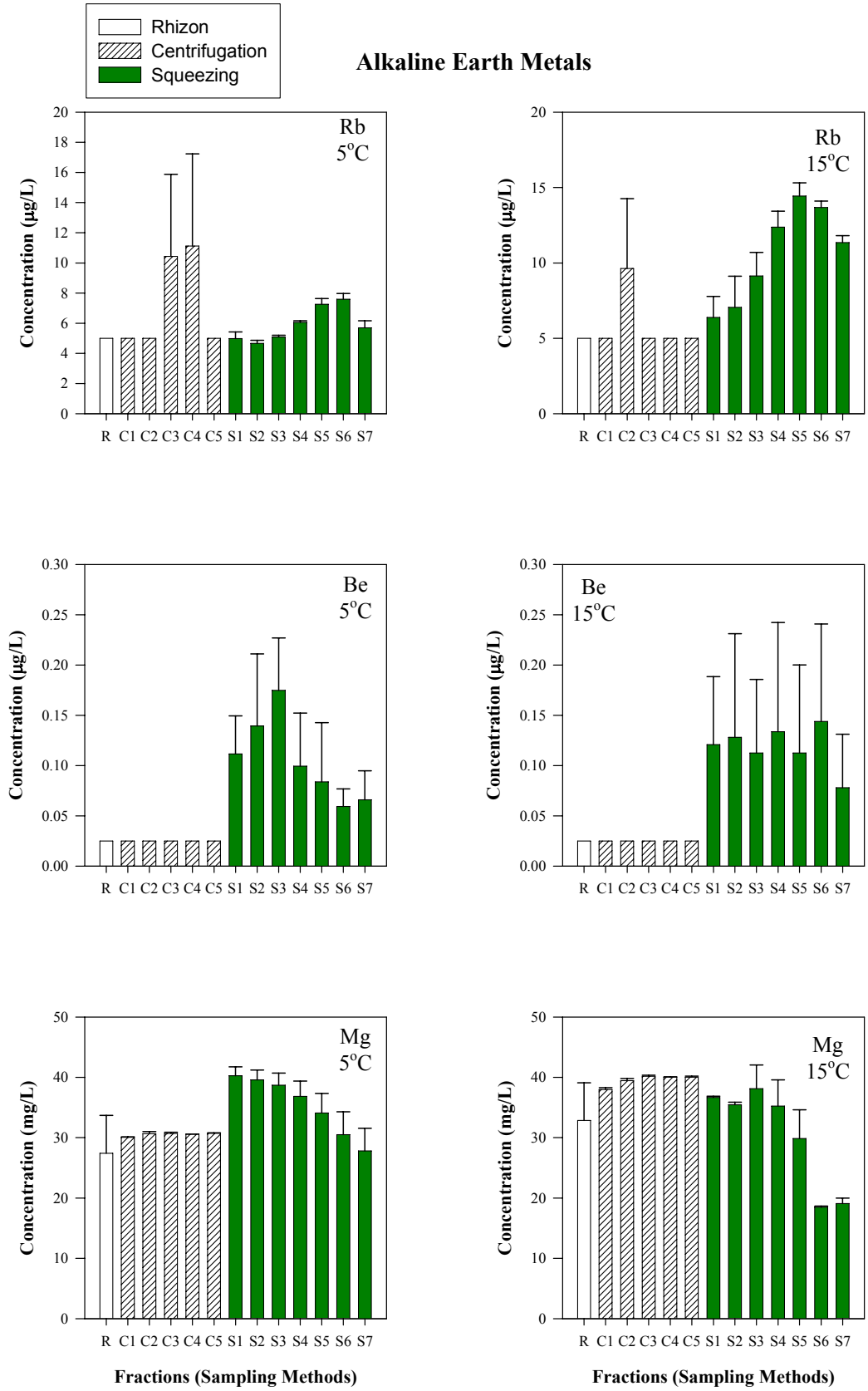


Figure 4.7. Element concentrations for pore water fractions at 5°C and 15°C for Stoke Bardolph: Alkaline Earth Metals; R = Rhizon samplers, C (1-5) = Centrifugation, S (1-7) = Squeezing; concentrations in mg L^{-1} or µg L^{-1} as stated.

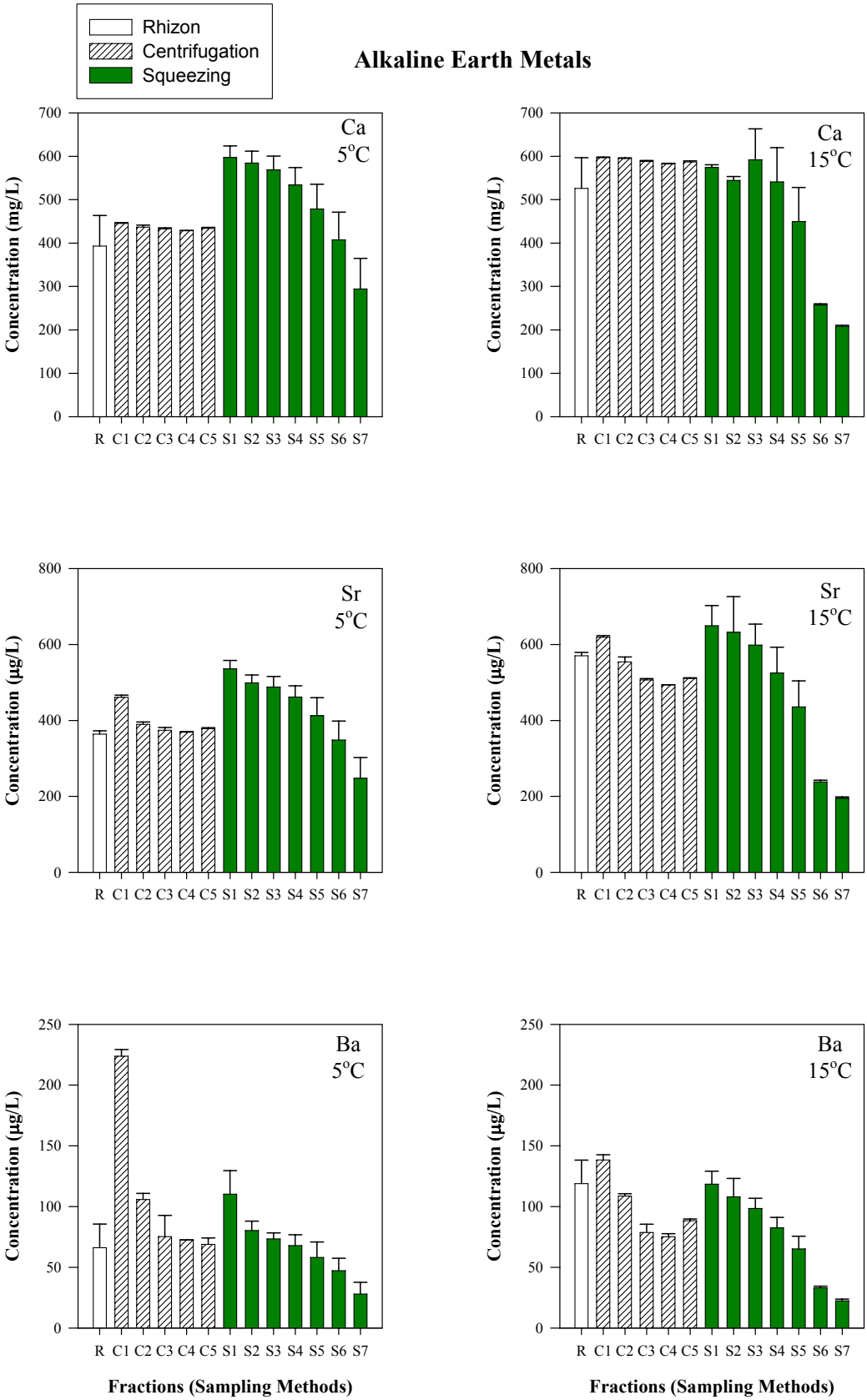


Figure 4.8. Element concentrations for pore water fractions at 5°C and 15°C for Stoke Bardolph: Alkaline Earth Metals; R = Rhizon samplers, C (1-5) = Centrifugation, S (1-7) = Squeezing; concentrations in mg L^{-1} or µg L^{-1} as stated.

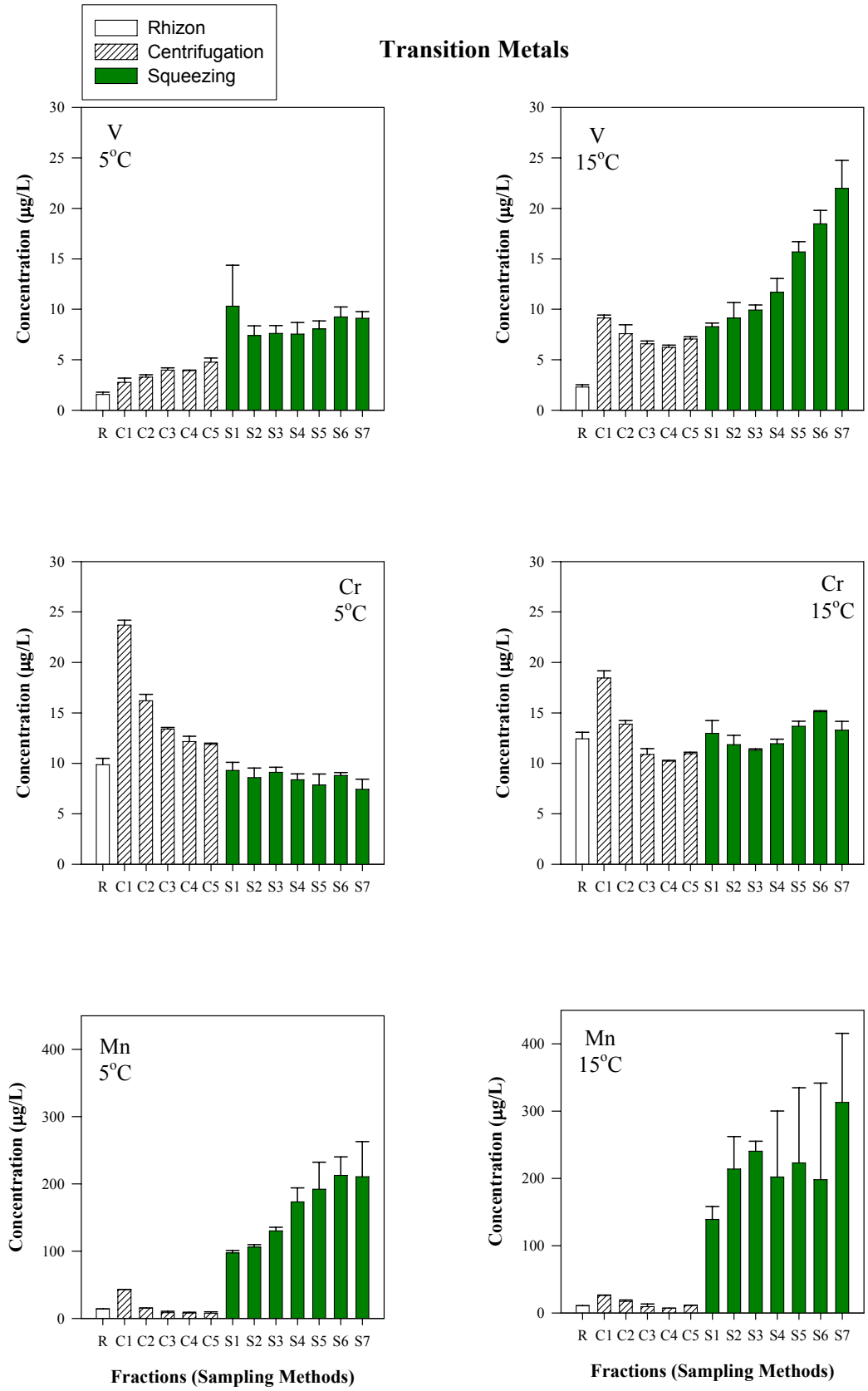


Figure 4.9. Element concentrations for pore water fractions at 5°C and 15°C for Stoke Bardolph: Transition Metals; R = Rhizon samplers, C (1-5) = Centrifugation, S (1-7) = Squeezing; concentrations in mg L^{-1} or µg L^{-1} as stated.

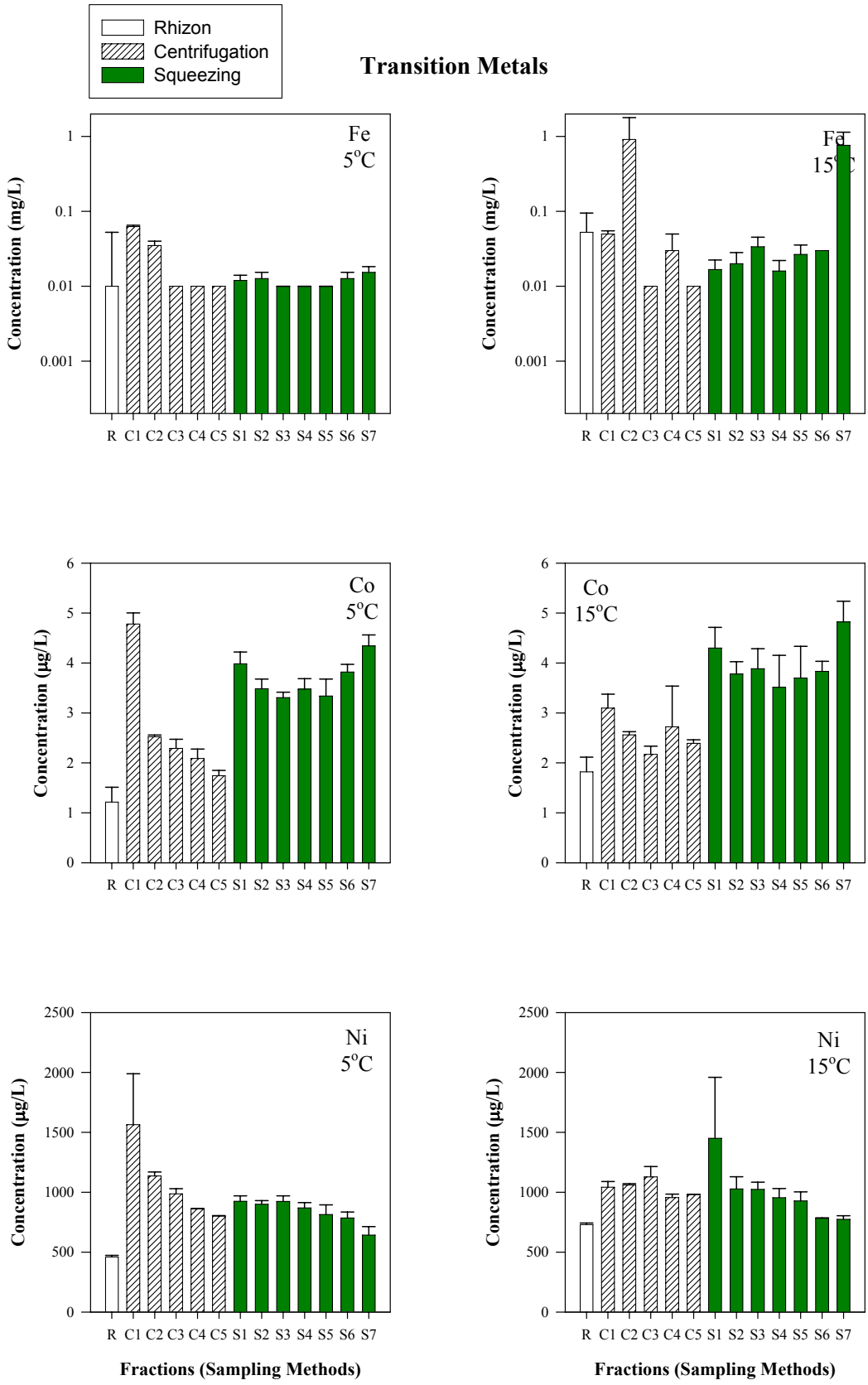


Figure 4.10. Element concentrations for pore water fractions at 5°C and 15°C for Stoke Bardolph: Transition Metals; R = Rhizon samplers, C (1-5) = Centrifugation, S (1-7) = Squeezing; concentrations in mg L^{-1} or µg L^{-1} as stated; NB: note logarithmic scale for Fe.

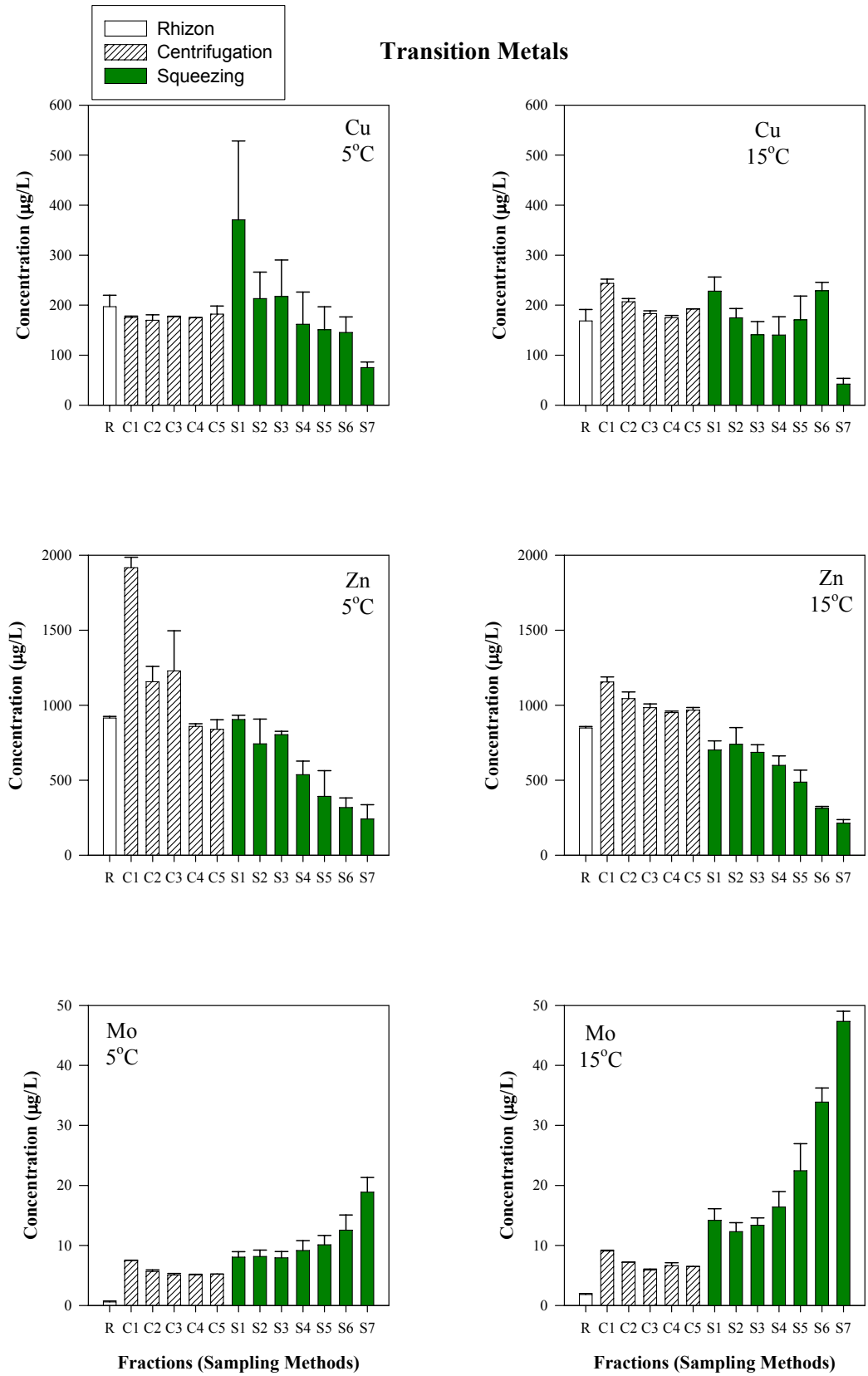


Figure 4.11. Element concentrations for pore water fractions at 5°C and 15°C for Stoke Bardolph: Transition Metals; R = Rhizon samplers, C (1-5) = Centrifugation, S (1-7) = Squeezing; concentrations in mg L^{-1} or µg L^{-1} as stated.

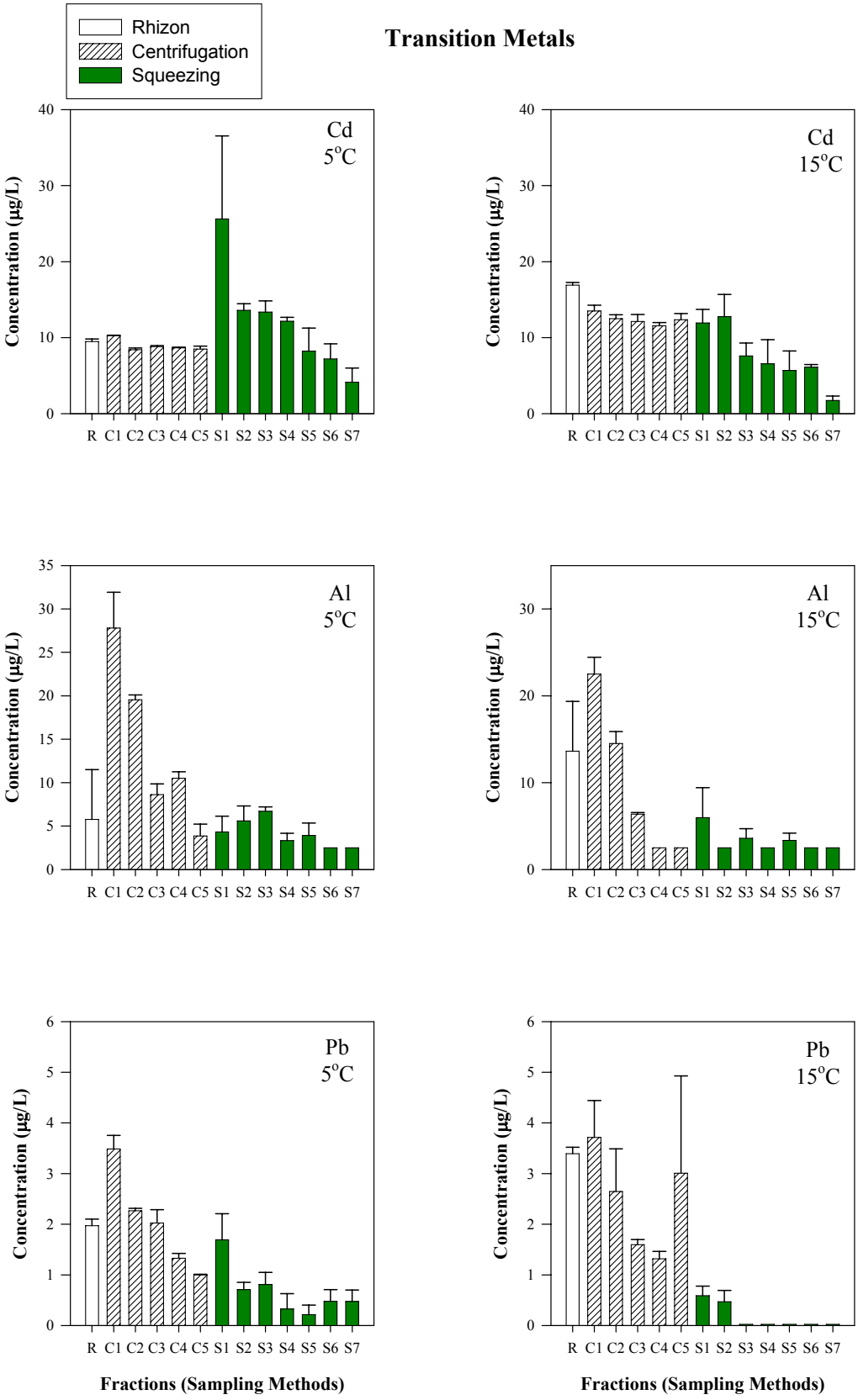


Figure 4.12. Element concentrations for pore water fractions at 5°C and 15°C for Stoke Bardolph: Transition Metals; R = Rhizon samplers, C (1-5) = Centrifugation, S (1-7) = Squeezing; concentrations in mg L^{-1} or µg L^{-1} as stated.

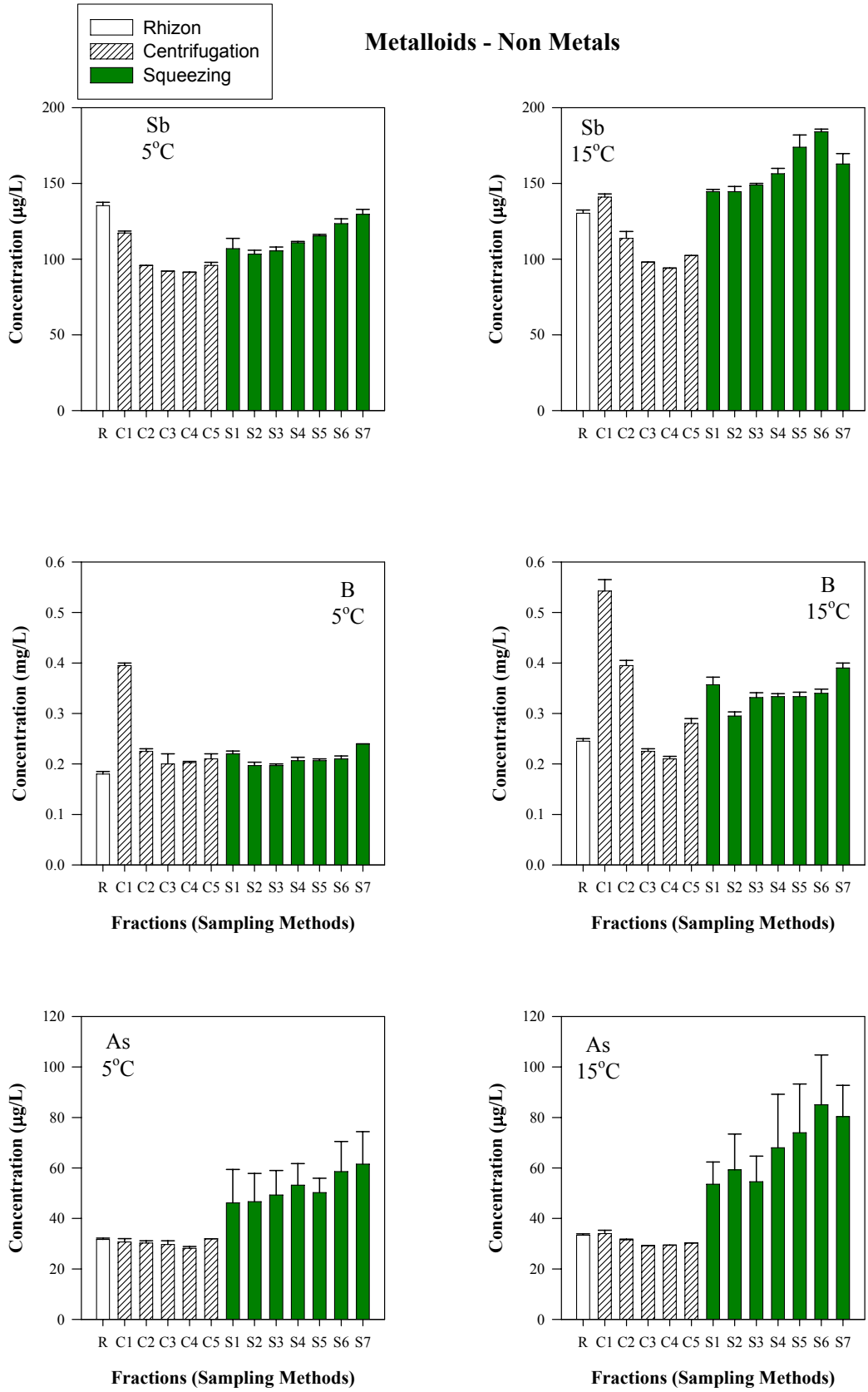


Figure 4.13. Element concentrations for pore water fractions at 5°C and 15°C for Stoke Bardolph: Metalloids and Non-Metals; R = Rhizon samplers, C (1-5) = Centrifugation, S (1-7) = Squeezing; concentrations in mg L^{-1} or µg L^{-1} as stated.

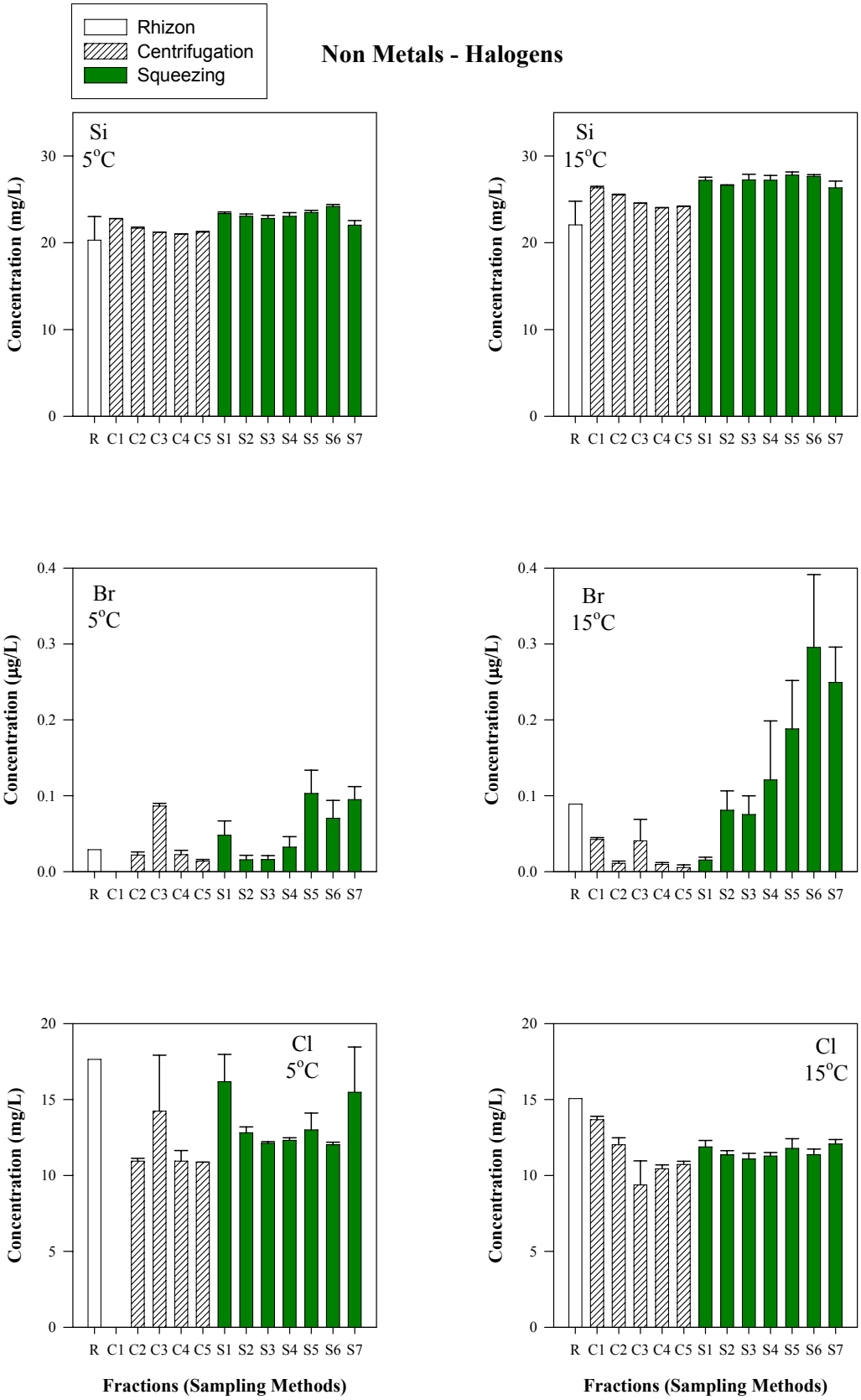


Figure 4.14. Element concentrations for pore water fractions at 5°C and 15°C for Stoke Bardolph: Non-Metals and Halogens; R = Rhizon samplers, C (1-5) = Centrifugation, S (1-7) = Squeezing; concentrations in mg L^{-1} or µg L^{-1} as stated.

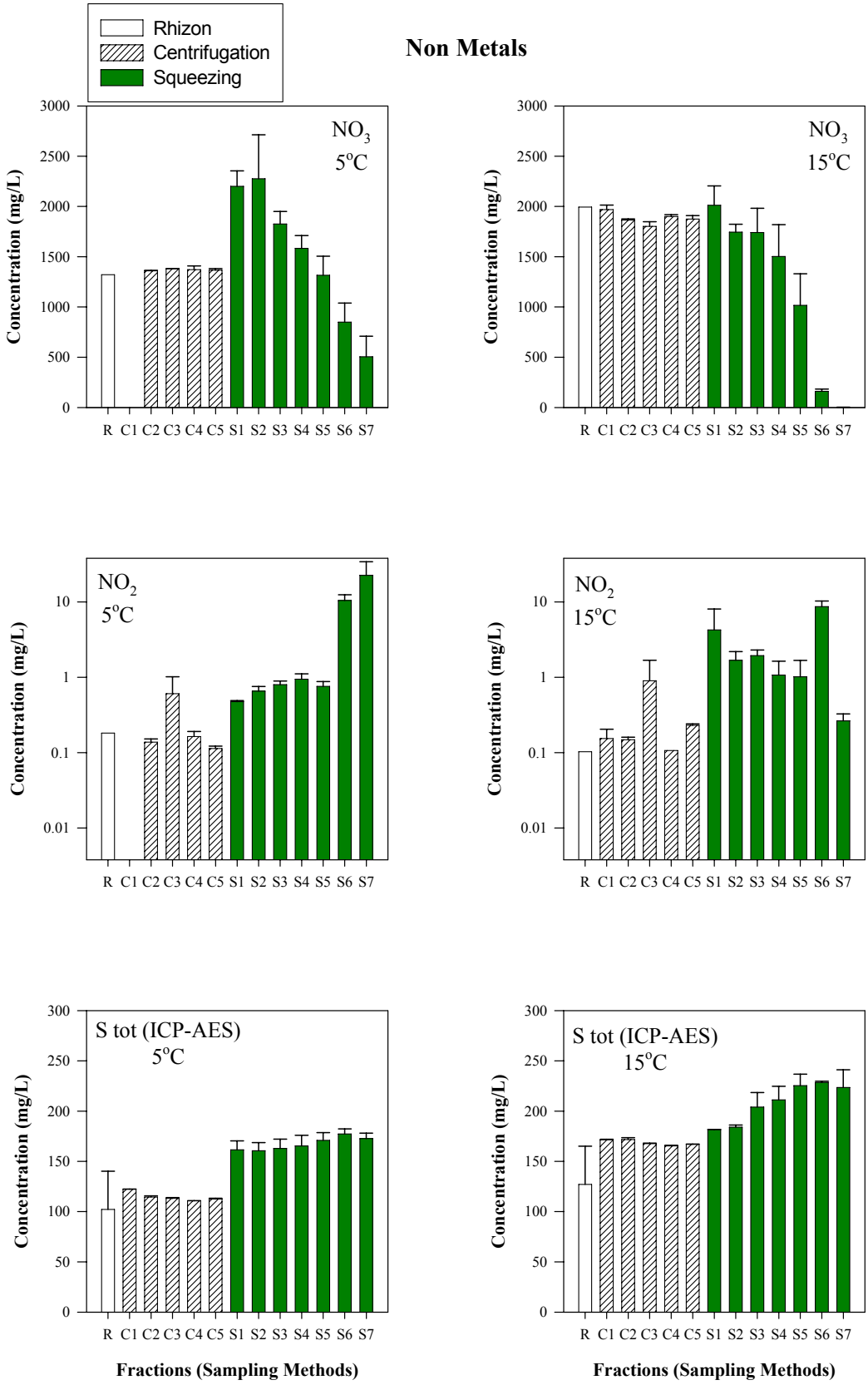


Figure 4.15. Element concentrations for pore water fractions at 5°C and 15°C for Stoke Bardolph: Non-Metals; R = Rhizon samplers, C (1-5) = Centrifugation, S (1-7) = Squeezing; concentrations in mg L^{-1} or µg L^{-1} as stated; NB: note logarithmic scale for NO_2.

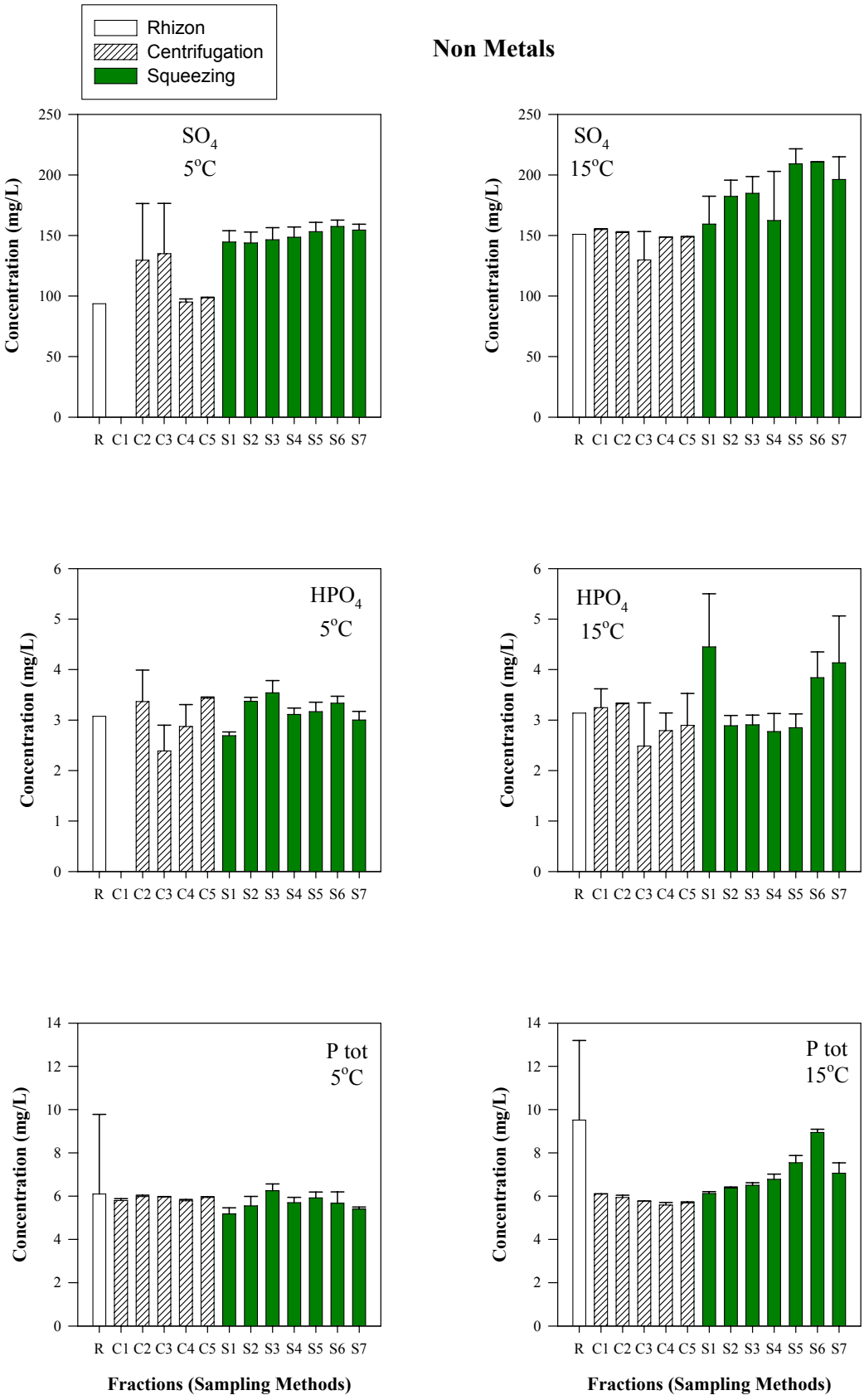


Figure 4.16. Element concentrations for pore water fractions at 5°C and 15°C for Stoke Bardolph: Non-Metals; R = Rhizon samplers, C (1-5) = Centrifugation, S (1-7) = Squeezing; concentrations in mg L^{-1} or µg L^{-1} as stated.

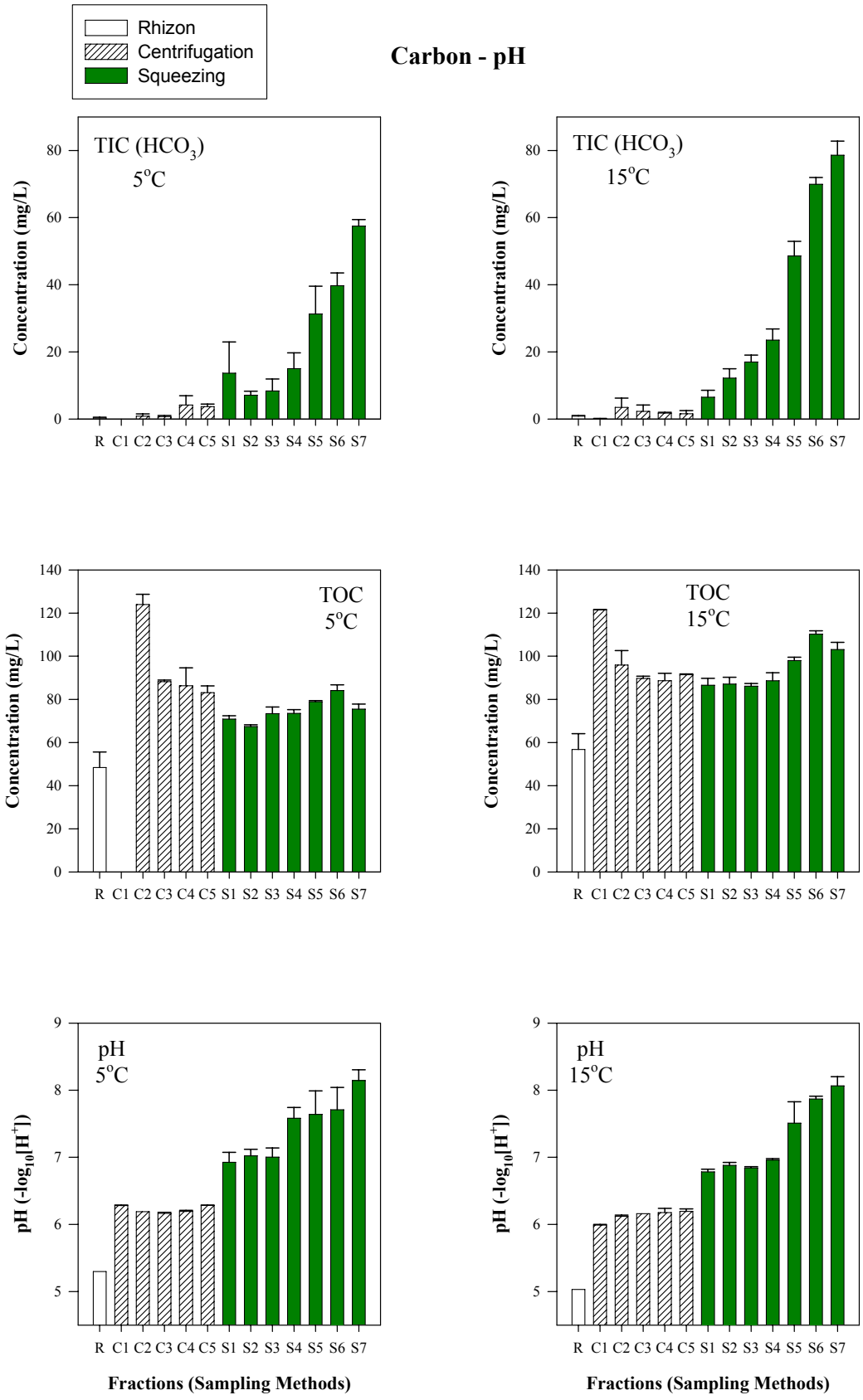


Figure 4.17. Element concentrations for pore water fractions at 5°C and 15°C for Stoke Bardolph: Organic, Inorganic Carbon and pH; R = Rhizon samplers, C (1-5) = Centrifugation, S (1-7) = Squeezing; concentrations in mg L^{-1} or µg L^{-1} as stated.

4.7.1.1. Ionic strength, pH and alkalinity

Comprehensive soil pore water analysis typically requires measurements of pH and total concentrations of major cations and anions that balance charge in the aqueous phase. The relationship between cations and anions is important in checking analytical results.

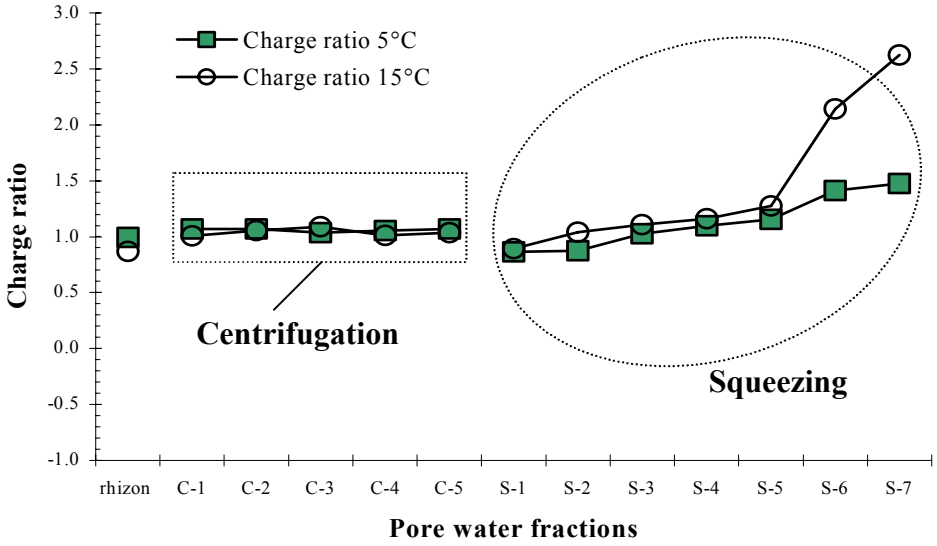


Figure 4.18. Charge ratio (cations/anions) in pore water fractions extracted by Rhizon samplers, centrifugation and squeezing as calculated by WHAM-VI; C = Centrifugation, S = Squeezing.

Ionic concentration can be examined through the difference of the sum of cations and anions, often referred to as *anion charge deficit* or through their ratio, which of course should be as close to 1 as possible. Figure 4.18 shows charge ratios for the soil pore water fractions as calculated by WHAM-VI. The WHAM picture of the pore water is somewhat different from the 'standard' one in which both inorganic and organic species (including FA and HA) are included (Tipping, 2002). WHAM considers the FA and HA as an electrically neutral phase, because any residual negative charge after specific binding is neutralised by counterions. In this way cations are not overestimated by omitting organic anions. Fig. 4.18 suggests that extracted

soil pore waters present a satisfactory electroneutrality over the whole range of samples, except towards the end of the squeezing extraction, where there appear to be an apparent excess of positive charge. This may be caused by the much smaller ionic strength (*I*) observed in these pore waters, giving a greater error in the calculation of the charge ratio.

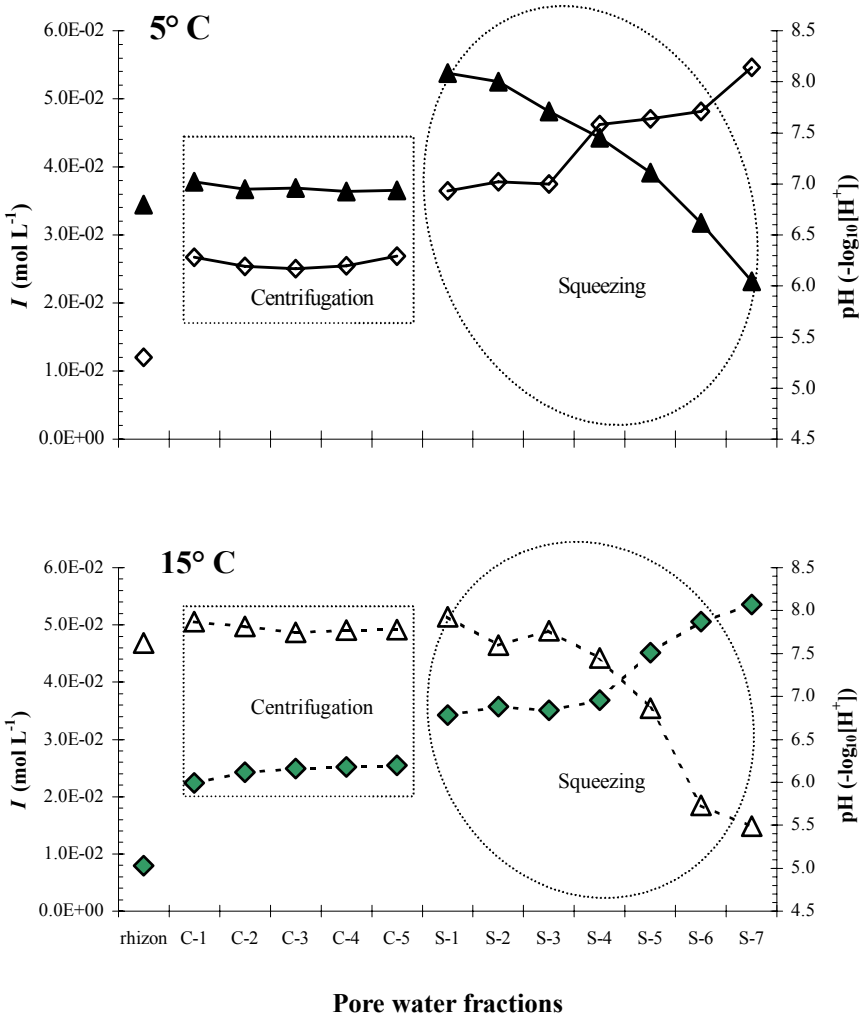


Figure 4.19. pH and ionic strength (*I*) for the pore water fractions extracted by Rhizon samplers, centrifugation and squeezing as calculated by WHAM-VI; triangles (▲;△) represent *I*, diamonds (◇;◆) represent pH.

In Fig. 4.19 *I* and pH are shown for each method of extraction, comparing how the major elements behave between the two datasets at 5 and 15°C. In both cases, *I* decreases significantly between S4 and S7. Although the soils were identical prior to extraction, *I* appeared significantly lower at 5°C

compared to 15°C for centrifugation; this difference is perhaps produced by the different response of the soil to temperature during extraction methods. Samples with a higher charge ratio (S4-S7) should be interpreted carefully and account taken of this imbalance, because some species may have been underestimated or could be missing from the calculations.

From Fig. 4.19 it is also evident that pore water pH appears to be significantly different for the 3 extraction methods. This finding is also supported by the variations in alkalinity, shown in Fig. 4.20 as calculated by WHAM-VI assuming measured DIC as master variable (calculations include charges on DOC).

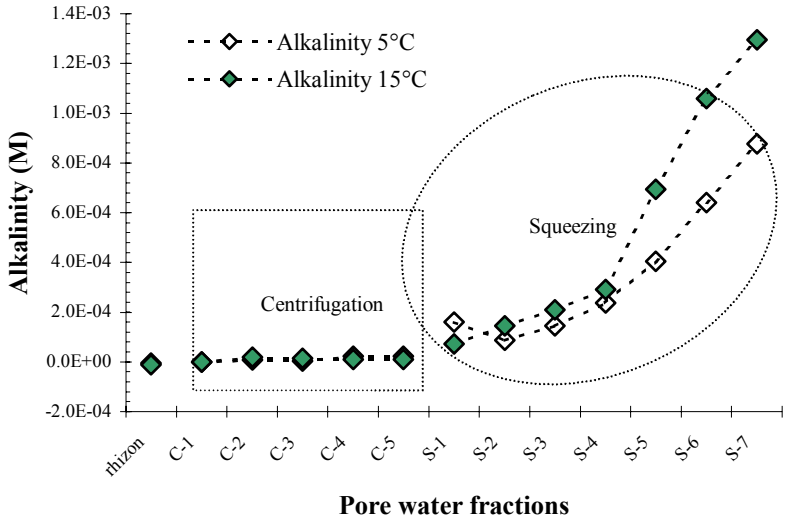


Figure 4.20. Alkalinity for the pore water fractions extracted by Rhizon samplers, centrifugation and squeezing as calculated by WHAM-VI.

These pH variations can have a major impact on many other pore water parameters, such as trace element solubility, bicarbonate concentrations and DOC. The pH plays a major role in regulating DIC levels by controlling the solubility of dissolved CO_2 through its control of the H_2CO_3 - HCO_3^- - CO_3^{2-} equilibrium. Dissolved hydroxyl (OH-), HCO_3^-, CO_3^{2-}, and organic matter all

increase in concentration as soil pH rises (McBride, 1994). Metal cation adsorption at mineral and organic surfaces is favoured at higher pH. Fulvic and humic acids dissolve leading to increased complexation by these ligands for some of the trace metals (e.g., Pb, Cu, Cr).

Lower pH values when using Rhizon samplers may be due to sampler preparation which consisted of an acid wash followed by deionised water rinses prior to use. As shown in Chapter 3 (see section 3.5.1), the surface of Rhizon samplers appears to be modified after a few extractions. Therefore, one possibility is that an organic coating (e.g. HA) may have formed on the external surface with a significant cation exchange capacity. The acid-washing stage of cleaning rhizon samplers would protonate such surface coatings. The resulting pool of exchangeable H^+ ions on the Rhizon surface would be unaffected by subsequent washing with deionised water but would exchange with soil pore water cations as the extracted solution passes through, resulting in a lower pH. Sorption of DOC on the surface of the Rhizon samplers could also explain the lower concentrations recovered (see Fig. 3.10).

Pore water pH for centrifuged samples was slightly higher than rhizon samples and remained constant throughout the extractions. During centrifugation the pore water is in contact with the soil throughout, which buffers the changes within the system due to pore water extraction (decrease in moisture content) and/or depletion in some elements. A similar situation could be expected for squeezing, except that pH (and so alkalinity) increased throughout. One of the possible reasons why the pH might increase is the uptake of protons by mineral weathering and ion-exchange reactions. At intermediate values of pH, carbonic and organic acids can readily attack and cause the dissolution of carbonates, silicates and alumino-silicates minerals in processes of chemical weathering, which increasingly consumes H^+ and CO_2, increasing alkalinity. As the water content decreases, the chemistry may

start to be dominated by mineral and solid phases (salts, bases or weak acids), with solubility reaction such as:

$$CaCO_3 \text{ (calcite)} + H^+ \rightleftharpoons Ca^{2+} + H_2O + CO_2$$

$$\underset{\text{K-feldspar}}{2KAlSi_3O_8} + 2CO_2 + 11H_2O \rightarrow \underset{\text{Kaolinite}}{Al_2Si_2O_5(OH)_4} + 2K^+ + 2HCO_3^-$$

with increasing pH. As a consequence, minerals that undergo weathering processes tend to decrease pCO_2 and can raise pH to values of 9 to 10 (Langmuir, 1997). Except for the increasing alkalinity however, this supposition is difficult to equate to available observations. It is much more likely that these variations in pH may be linked to changing redox conditions. Reduction reactions such as NO_3^- reduction (denitrification) imposed by depletion of oxygen by microorganisms or biological immobilization over the longer time required for the squeezing extraction, generally consume H^+ ions. Reactions such as:

$$5CH_2O + 4NO_3^- + 4H^+ \rightarrow 5CO_2 + 2N_2 + 7H_2O$$

$$NO_3 + 2H+ + 2CH_2O \rightarrow NH_4^+ + 2CO_2 + H_2O$$

where CH_2O represents organic matter (i.e. glucose, cellulose), are likely to occur when anaerobic conditions prevail, i.e. as the system, unable to exchange with atmosphere, starts to deplete oxygen by aerobic decay and microbial respiration.

4.7.1.2. Organic carbon

Another reason why centrifugation and squeezing generally present higher trace element concentrations (and/or greater anion deficit) could be the presence of dissociated organic acids. The extracted pore waters presented greater DOC concentrations in the centrifuged and squeezed

samples compared to Rhizon samples (Fig. 4.21). Samples from centrifugation showed a steady decrease in concentrations with increasing speed (i.e. pressure) applied, whereas DOC in squeezed samples increases with increasing pressure, starting from S4. The greater DOC concentrations found in the early stages of the centrifugation for the soil studied, could explain the very similar behaviour of some elements during these extractions by centrifugation (Cr, Pb, Na, K, Sr, Ba, Mn, Co, Zn, Al, Sb, Cu at 15°C and Ni at 5°C, see Fig. 4.6 – 4.17), whose concentrations mirrored that of DOC which in turn could enhance their solubility. Different mechanisms could explain why the same is not observed during the later stages of squeezing. The pressures applied are much greater, the sample is at low moisture content, and DIC increases drastically, which is coupled with an increase in pH and changes in redox conditions (see section 4.7.3). These conditions may favour adsorption on the solid phase within the smaller spaces where water remains during those stages of squeezing.

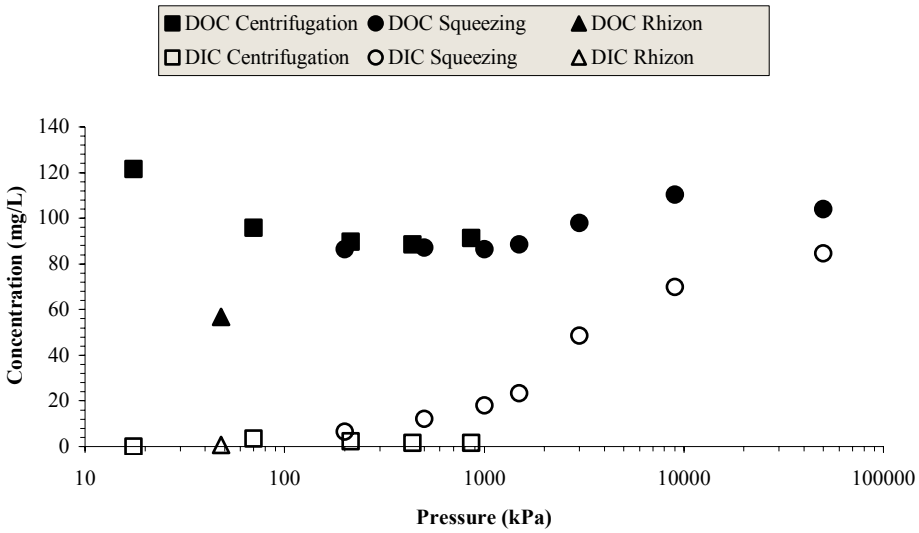


Figure 4.21. Organic and inorganic carbon concentrations with increasing pressure applied during pore water extractions at 15°C.

Reasons for higher DOC concentrations are sometimes attributed to rupturing of biological tissues during centrifugation (Ross and Bartlett, 1990;

Lorenz *et al*., 1994). This would also be expected for squeezing due to the destructive nature of the two methods. However, there are studies in which centrifugation was applied that contradict this view (Zabowski, 1989; Zabowski and Ugolini, 1990). Total organic C concentrations decreased with increasing pressure applied when pressures from 15 to 948 kPa were used (Grieve, 1996), but blockage of the filters in later extraction steps may have accounted for the reduction in DOC concentrations, with an easier passage of fine particulate carbon in the early stages of the extraction. Sheppard *et al*., (1992) found different effects of centrifuge speed over organic and mineral soils, with anions being more affected than cations. However, for organic soil higher centrifugation speeds produced higher concentrations for all the elements (major anions and cations) considered except Fe.

4.7.2. Conditions applied during the extraction

4.7.2.1. Pressure and temperature

Both applied pressure and temperature may be important variables during pore water extraction. The effect of pressure seems to be negligible when driving pressures are < 4.5 MPa (Wolt, 1994). An increase in pressure leads to an increase of K_w, the dissociation constant of water, hence pK_w will decrease, with possible implications for the pH of the system ($pH = pK_w - pOH$). Centrifuged and squeezed samples show greater cation concentrations compared to rhizon sampling (Fig. 4.6 – 4.17). This could be explained by the different magnitude of pressures (suction) applied as suggested by previous studies comparing centrifugation and lysimeters (Zabowski and Ugolini, 1990, Giesler *et al*., 1996). It is possible that the pressure applied could affect the solubility of some of the minerals occurring in the solid phase, enhancing processes of chemical weathering or altering the conditions or mineral dissolution/precipitation.

It is also well known that solubility products are dependent on temperature. An example of the effect of pressure and temperature is shown

in Fig. 4.22, where calculated saturation indices (SI) are shown for carbonate minerals, where values > 0 indicate mineral precipitation, values < 0 indicate mineral dissolution. Differences caused by the incubation temperature may have affected centrifuged samples. By contrast, for squeezed samples data are very similar for both treatments (with the exception of siderite).

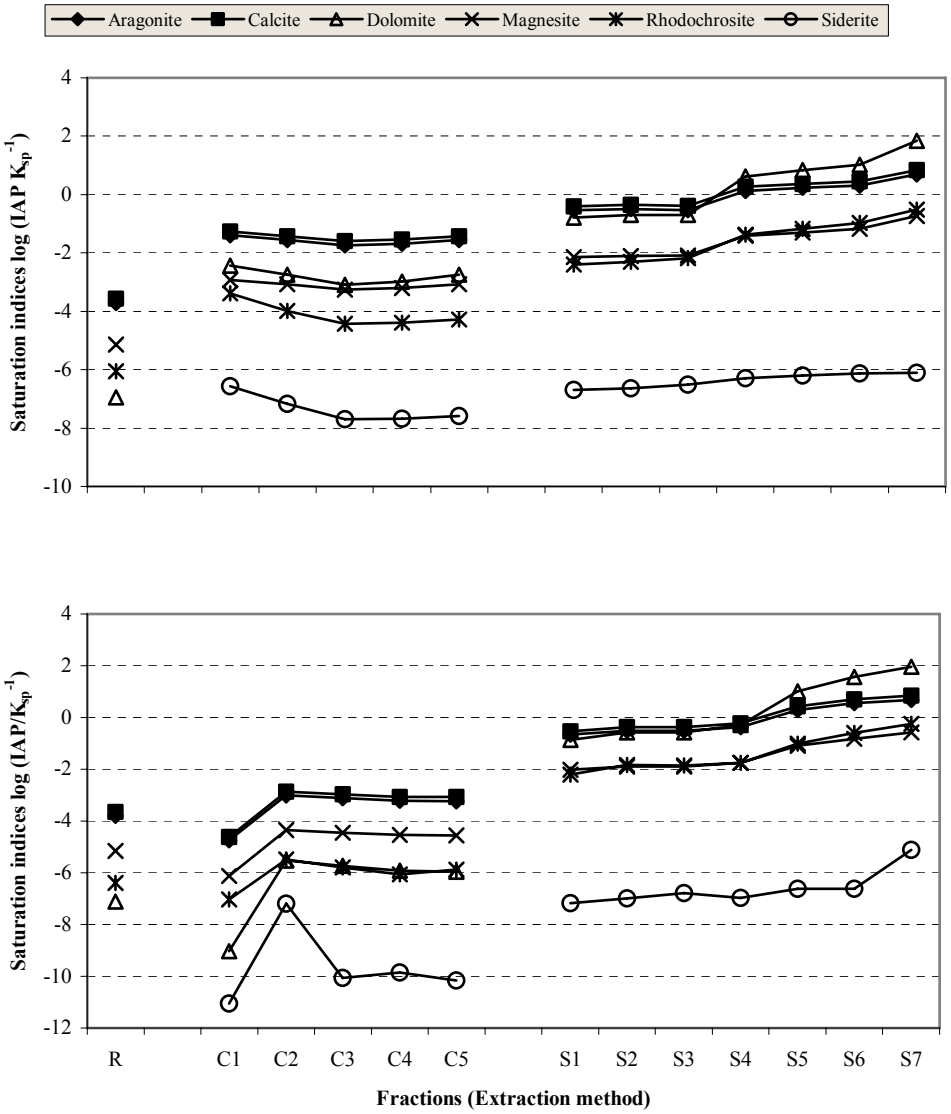


Figure 4.22. Saturation Indices for carbonate minerals as calculated from soil pore water compositions using PHREEQCi (database Llnl), at 5° (top) and 15°C (bottom). IAP = Ion Activity Product; K_{sp} = Solubility product.

Furthermore, data show undersaturation or near-equilibrium conditions for carbonate minerals in both rhizon and centrifugation samples. Squeezed samples show near-equilibrium but variable SI values, for dolomite and aragonite; the latter is an unlikely mineral in surface conditions. Conditions for calcite were apparently supersaturated from S4 onwards.

Data (not shown) suggest that the sulphate mineral jarosite is always grossly undersaturated; by contrast anhydrite and gypsum are slightly undersaturated whereas barite is slightly supersaturated. Alunite shows instead a variable SI, with decreasing values both during centrifugation and squeezing. Similar results were found for Fe, Mn and PO_4 phases (data not shown).

Speciation of all pore water components is affected directly by pressure and temperature during displacement and indirectly by pressure and temperature-induced shifts in pore water pH. Composition of the pore water obtained may be altered to the extent that mass is transferred between pore water and other soil phases (mineral, organic and gaseous) during the displacement. In other words, failure to achieve a system model for soil pore water in which pressure and temperature are constant during the period of displacement may invalidate or make more difficult the interpretation of the results arising from the displacement.

4.7.2.2. Compaction and porosity

During both centrifugation and squeezing, there is considerable destruction of the initial soil structure (although soil samples were not undisturbed in the first place). It is likely that during the extractions when using these methods, some degree of reorganization of soil particles occurs, with larger spaces being progressively disrupted (compaction). At the pressures applied here, the soil structure is of less importance for water retention (Hillel, 1982) than its texture. The reorganization of soil particles and breakage of aggregate structures may also expose mineral surface areas

and a range of ion-exchange sites to the pore water which is different from those under initial conditions or under the conditions occurring under rhizon sampler extraction. In this case, however, the contact time between the soil and the pore water is another important factor to account for any chemical processes likely to affect the composition of the extracted pore water.

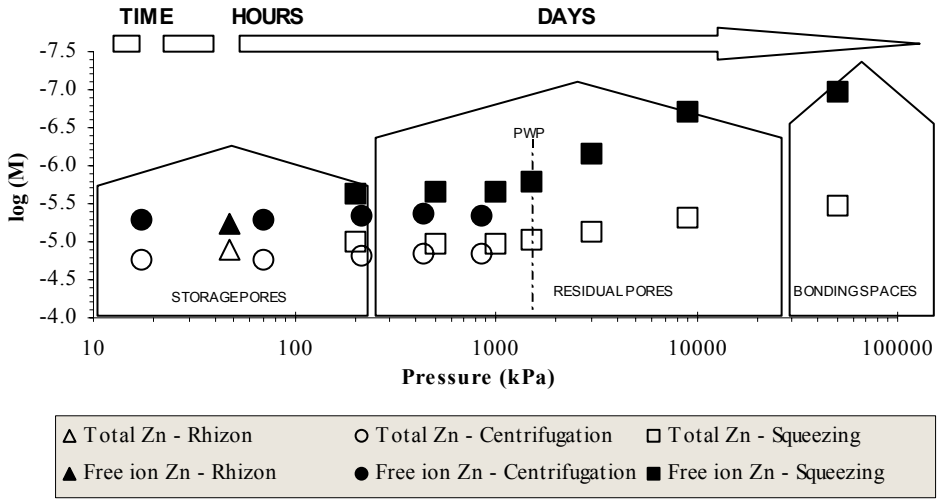


Figure 4.23. Total and free ion activities (determined by WHAM-VI) of Zn in soil pore waters extracted at 5°C compared with the pore diameters equivalent to the pressures applied with the three methods. PWP = Permanent Wilting Point; classification of pores after Greenland and Hayes, 1981; Time scale qualitative.

Non-equilibrium conditions during chemical transfer between different pore classes may affect the extracted pore water composition (Luxmore *et al.*, 1990, Cozzarelli *et al.*, 1987), (Fig. 4.23). However, for the reasons explained in chapter 3, it is difficult to ascribe the origin of soil water collected at one or more pressures using devices such as rhizon samplers, whereas the source of water sampled by centrifugation and squeezing is more reliably known, if not in relation to pore size classes, at least in terms of the volume of soil sampled.

Adams *et al.*, (1980) found different pore water Al concentration when comparing centrifugation and column displacement techniques. The

sequential 'stripping' of pore water both using centrifugation and squeezing by increasingly strong pressures (forces) could gradually increase the importance of the micropores and one could argue that less available water is gradually released and collected. Differences in (major) element concentration among pore water fractions at different pressure applied (expressed as relative centrifugal force – RCF) were studied on a calcareous soil by Tyler (2000). The largest concentrations for most elements analysed were measured in the fraction held by very weak forces (RCF ≤ 24), whereas concentrations were lowest in pore water expelled at high pressures. Only P and Mo amongst the elements studied showed an inverted pattern (i.e., highest concentrations in micropores or higher pressures). These results were explained by an apparent displacement of ion equilibria in the micropores towards the solid phase; however, the reasoning behind this it is not clear, especially considering that in those circumstances the soil would increasingly buffer the solution. Comparisons of pore water concentrations in relation to pore sizes are not always conclusive. For example, when a tracer (bromide) was used to define the variation in soil solute concentration (Harvey, 1983), no sharp change was detected at the macropore-micropore breakpoint in effective size to suggest a division in concentration into two corresponding transport domains, in spite of the well-defined division in pore size classes determined by water retention criteria. The same conclusion was reached when using micro soil pore water sampling devices similar to rhizon samplers (Spangenberg *et al*., 1997), where measured concentration did not seem to be a function of pore size or strength of suction applied to the sampler types, as suggested by Grossmann and Udluft (1991). Essert and Hopmans (1998) noticed an increase in Cl concentrations (used as a tracer because it is a conservative ion) with increasing suction applied to their extraction device. They argued that, as suction corresponds to soil water pressure decrements, the size of the water-filled pores decreases: as a result, pore water concentration (for Cl) is higher in smaller solution-filled pores.

The explanation given for this increment was 'anion exclusion', as the relative exclusion volume increases with decreasing soil water content. With 'anion exclusion', the average transport velocity of dissolved anions through soils may be larger than that of the accompanying water molecules, owing to electrostatic repulsion by negatively charged solid surfaces, which forces the anions into pore centres where the velocity is faster. This phenomenon has been explained by diffusive double-layer theory (Dzombak and Morel, 1990) and results indicate that anion exclusion restricts the number of active pore networks available for anion transport (Gvirtzman and Gorelick, 1991). Pore water compositions from centrifugation and squeezing do not rule out the effect of anion exclusion, since trends show minor increases of Cl^-, SO_4^{2-}, Br^-, as well as Mo, V and As (usually occurring as anions) concentrations at increasing pressures. The evidence however is not compelling, therefore no conclusions are drawn in this direction.

4.7.2.3. Moisture content

Another variable to consider as a possible reason for the variation in solute concentration is the change in moisture content that occurs during the multiple-step extractions. Both centrifugation and more markedly squeezing extraction produced several samples; as a result the latter stages of each technique include samples of pore water from below-FC environments. Jones and Edwards (1993) argued that if solute concentration was a function of moisture content, and solid phase exchange reactions occurred rapidly, changes may take place in solute composition during its passage through the sample. However, they found that pore water composition of successively extracted fractions showed no concentration differences, concluding that minimal interference from the charged solid phase occurs when solution passes through the sample. On the other hand, a larger moisture content restricts gas diffusion and decreases the partial pressure of O_2 and increases the partial pressure of CO_2 due to biological activity (Magnusson, 1992). A

larger partial pressure of CO_2 would again promote chemical weathering, which constitutes one of the major sources of base cations in soils. Liberation of base cations through chemical weathering increases the alkalinity of soil pore water, which is observed especially during the later stages of squeezing extraction.

4.7.3. Chemical reactions and redox conditions

Stable Eh measurements are only possible in well-poised systems. Such systems, which are described as having high redox capacity, tend to resist changes in Eh, due to the presence of species of Fe, S and Mn which can buffer the redox potential. This is likely to be the situation for the soil sample during centrifugation, where those species are actually buffering the system against changes in redox conditions (Fig. 4.24).

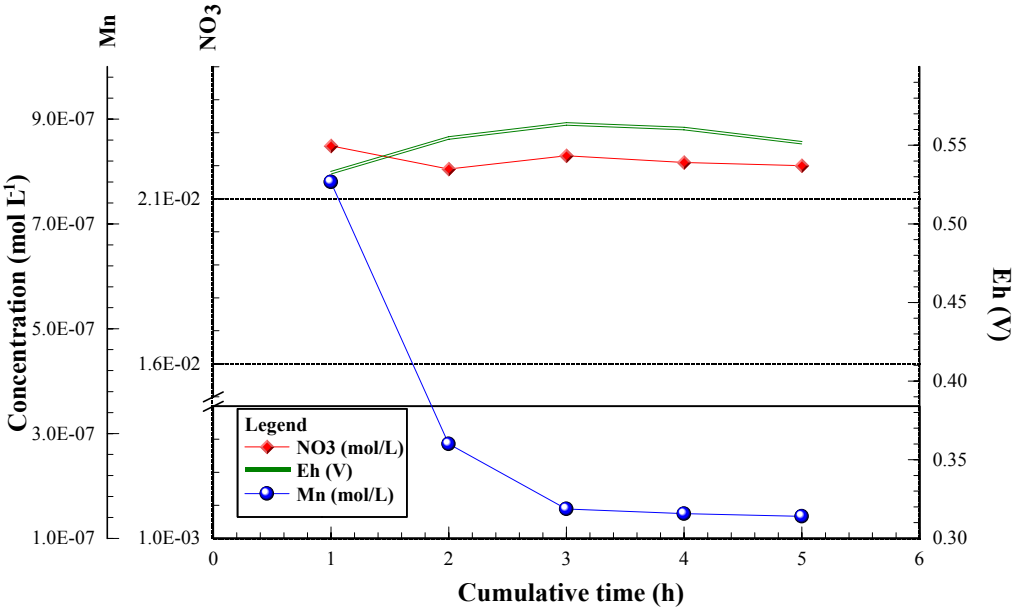


Figure 4.24. Concentrations of Mn and NO_3^- in solution compared to calculated Eh during centrifugation extraction at 5°C.

Even hypothesising that equilibrium is not maintained during centrifugation, this extraction method, with its stop-and-go procedure, theoretically allows

the sample to re-equilibrate with atmosphere. However, the much shorter extraction time is probably more important in this respect.

By contrast, in anaerobic systems, Eh measurements may be stable and meaningful only if species of Fe, S and Mn dominate the redox chemistry. During squeezing there could be completely different conditions compared to centrifugation. Here the sample is not in contact with atmosphere and oxygen is possibly depleted during the extraction. Furthermore the sample is under these conditions for a much longer period of time compared to centrifugation since squeezing proceeds for several (4 - 5) weeks. If decaying organic matter is part of a system that has been isolated from atmospheric oxygen, normally, this will be the major reductant. In these conditions aerobic decay takes place first, depleting all free O_2, after which, as the Eh drops, anaerobic conditions are established, with NO_3^- and MnO_2 being the first species to be reduced. Atmospheric oxygen is relatively insoluble in water, making it easier to deplete the dissolved oxygen content of water. NO_3^-will be progressively depleted as an alternative electron acceptor and Mn^{2+} is increasingly released into solution as the redox potential falls (see Fig. 4.25). Furthermore, unsaturated soil moisture is usually oxygen-saturated (aerobic), except in soil microenvironments rich in organic matter (Langmuir, 1997). Hence one could argue that as the squeezing process progresses, extracted samples contain greater contributions from progressively smaller pores (i.e. soil particles rearrange and only smaller spaces are remaining) with their different microenvironments, and hence possible different redox conditions.

Table 4.7 lists the Eh values and the equivalent pe calculated using this approach for both temperatures. There is a difference in the range of Eh values between the two temperatures, due to the different values of (Mn^{2+}) – as calculated by WHAM - in solution and different pH. The values for centrifuged samples appear to be almost constant throughout the extraction, whereas Eh clearly decreased during squeezing.

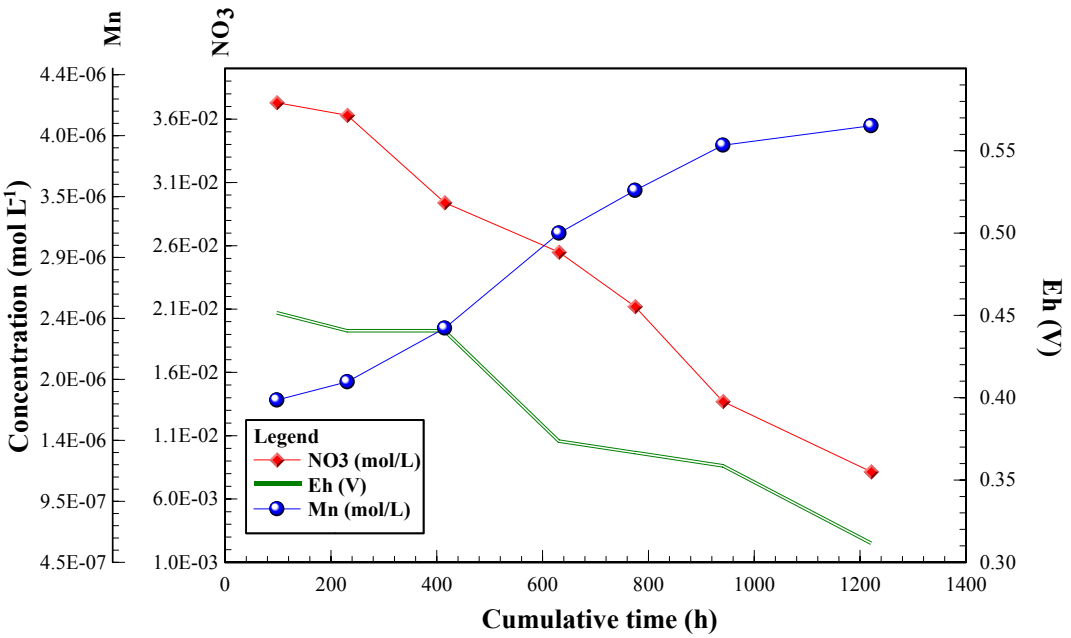


Figure 4.25. Concentrations of Mn and NO_3^- in solution compared to calculated Eh during squeezing extraction at 5°C.

Comparing these calculated values with the redox ladder shown in Table 4.2, one can see that as Eh (pe) of the soil pore water dropped below +0.607 V (pe = +11), enough electrons become available to reduce $O_2(g)$ to $H_2O(\ell)$. This is the case for centrifuged samples at 5°C but not at 15°C, although, even at the lower temperature, values of Eh do not vary significantly during centrifugation. As pore water samples were collected by squeezing, Eh droped below +0.441 V (pe = +8): in this case electrons become available to reduce NO_3^-. This reduction is catalysed by nitrate respiration involving bacteria that ultimately excrete NO_3^-, N_2, N_2O or NH_4^+. In addition, it has to be noted that squeezed samples already had a lower starting Eh compared to centrifuged and rhizon samples, corresponding to a slightly higher pH and higher (Mn^{2+}) observed during squeezing.

Table 4.7. Eh and equivalent pe values for the pore water fractions at 5° C and 15° C as calculated using equations (4.4) and (4.5); free ion activities are reported as calculated by WHAM VI.

Sample	(Mn^{2+}) (M)	pe	Eh (V)	(Mn^{2+}) (M)	pe	Eh (V)
		5°C			15°C	
R	1.30E-07	11.8	0.652	9.06E-08	13.3	0.735
C1	3.09E-07	9.67	0.533	1.93E-07	11.2	0.620
C2	1.13E-07	10.1	0.555	1.22E-07	11.1	0.611
C3	6.76E-08	10.2	0.564	8.06E-08	11.1	0.612
C4	6.38E-08	10.2	0.561	5.20E-08	11.1	0.615
C5	6.06E-08	10.0	0.552	8.52E-08	11.0	0.607
S1	6.86E-07	8.19	0.452	9.97E-07	9.30	0.513
S2	7.36E-07	8.00	0.441	1.61E-06	9.00	0.496
S3	9.10E-07	7.99	0.441	1.73E-06	9.06	0.500
S4	1.12E-06	6.78	0.374	1.37E-06	8.87	0.489
S5	1.19E-06	6.65	0.367	1.37E-06	7.77	0.429
S6	1.25E-06	6.50	0.359	9.99E-07	7.12	0.393
S7	1.13E-06	5.66	0.312	1.36E-06	6.65	0.367

R = Rhizon; C = Centrifugation; S = Squeezing

In the later stages of squeezing, Eh values dropped to between +0.386 and +0.276 (corresponding to pe 7 and 5), where sufficient electron donors are available to support the reduction of Fe and Mn in solid phases. Iron reduction does not occur until O_2 and NO_3^- are depleted, but Mn reduction can be initiated in the presence of nitrate. This is confirmed by the fact that Fe did not appear to contribute to the solution phases during this phase.

The formation of reduced species (reduction) represents a mechanism by which free protons are consumed and removed from soil pore water, resulting in an increase in pH which clearly manifested during squeezing (see Fig. 4.19). Furthermore, the time variable is also very important during redox reactions. They are often extremely slow and require catalytic processes mediated by microbial organisms to occur. In the case of a chemical system not able to exchange with atmosphere (i.e. closed system) that is maintained for a prolonged period of time (i.e. during squeezing), redox reactions will be controlled by the behaviour of the system itself that is

catalysed effectively by bacteria, which will increase the rate of redox reactions.

Figures 4.24 and 4.25 outline these different Eh variations between centrifugation and squeezing compared to the corresponding concentrations of the main species involved in the calculation (i.e. Mn and NO_3^-).

4.7.4. Trace elements and species variation

Different or varying redox conditions may lead to different concentration and speciation of trace elements in soil pore water. Transition metals such as Ni, Zn, Cd, Pb and metals like Al, present similar behaviour at the two temperatures, showing a progressive decrease in solution concentration with both centrifugation and squeezing, more markedly during squeezing. Their speciation however, calculated with WHAM-VI show different fractions of the available species (free ion) and the complexed forms.

4.7.4.1. Cadmium

Fig. 4.26 shows Cd speciation at 5°C and at 15°C. The combination of a much lower concentration of DOC and pH values found in rhizon samples creates a much higher proportion of Cd^{2+} in the total Cd concentration (~90%). Conversely the proportion of Cd bound to HA and FA (here presented together) increases significantly over the course of centrifugation extraction, where values remain constantly around 25-30% of the total. During squeezing the amount of organically bound Cd increases substantially (up to 70%) as the pH rises and DOC concentrations increase, at the expense of Cd^{2+}. This is in line with the lower concentrations recorded and the general observation that Cd is more mobile at lower pH, whereas at more alkaline pH, Cd solubility and availability is limited by the stronger absorbance to OM, clays and oxides, as well as co-precipitation with $CaCO_3$ or precipitation as $CdCO_3$.

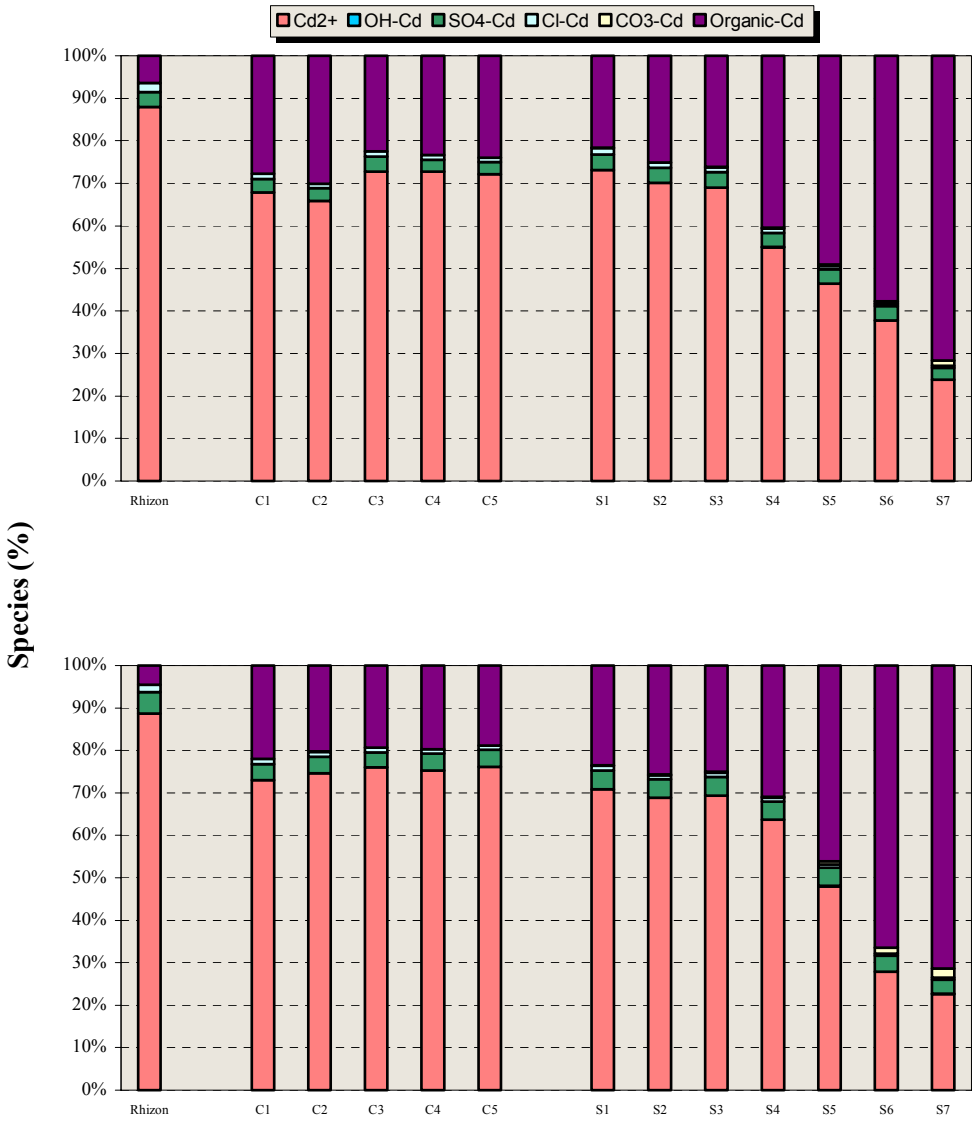


Figure 4.26. Cadmium speciation at 5°C and 15°C for the three extraction methods; Ligands are grouped in categories: Organic = HA and FA; CO_3 = carbonatic ligands; OH = oxy-hydroxyl ligands.

4.7.4.2. Zinc, Nickel and Cobalt

Very similar behaviour to Cd is shown by Zn. However, there is a difference between the respective proportions of free Zn^{2+} and metal bound to HA and FA at the two temperatures (Fig. 4.27), which is particularly evident for the centrifugated samples. At 5°C they almost share the same abundance in solution (45-50%), whereas at 15°C the free ion Zn^{2+} is presents at a higher relative concentration (~60%) over Organic-Zn (~40%).

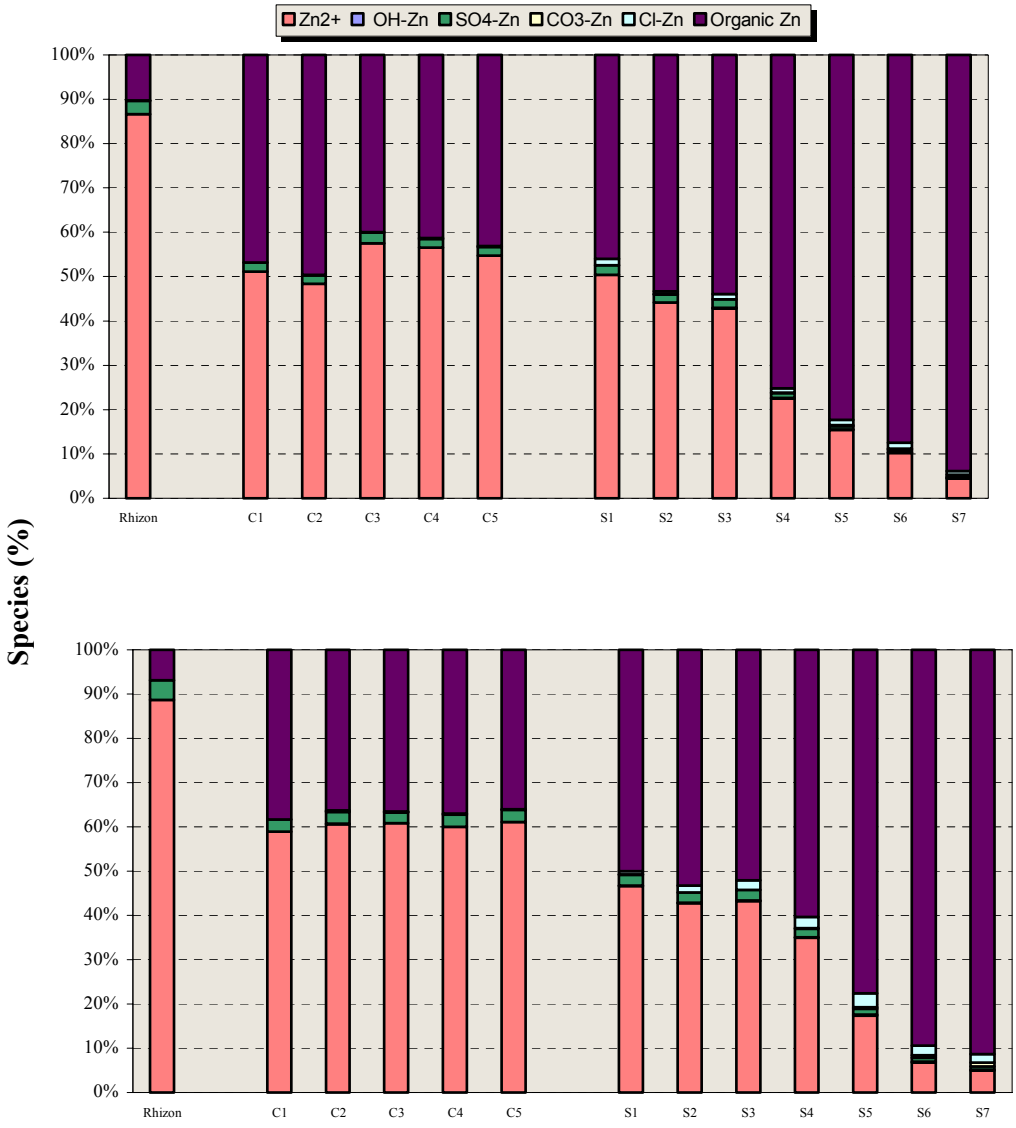


Figure 4.27. Zinc speciation at 5°C and 15°C for the three extraction methods; Ligands are grouped in categories: Organic = HA and FA; CO_3 = carbonatic ligands; OH = oxy-hydroxyl ligands.

Nickel concentrations in solution are comparable with those of Zn across the 3 extraction methods, not only because they decrease along extractions but also in terms of magnitude (Fig. 4.28). However calculated speciation shows a different behaviour, because inorganic ligand competition with DOC is more important.

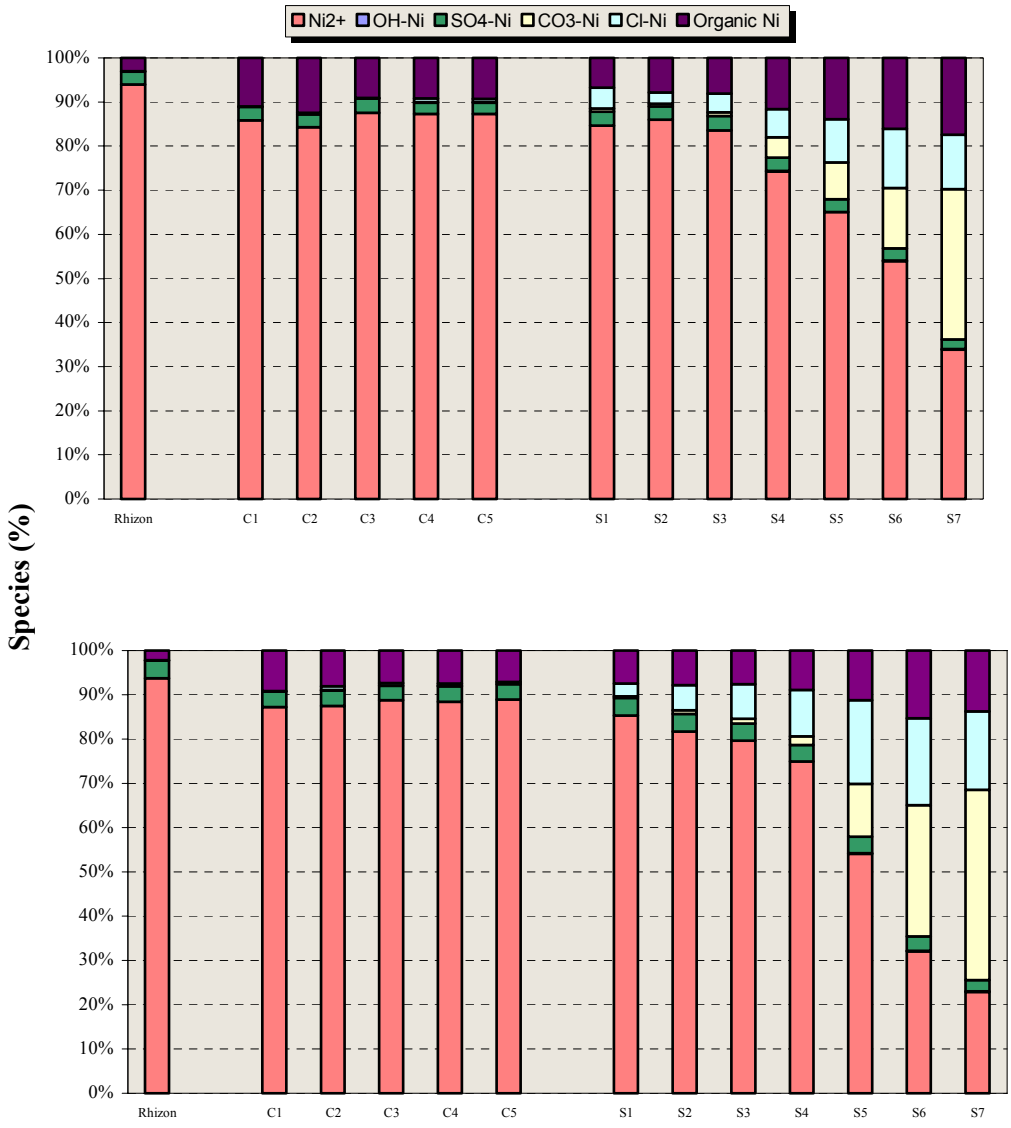


Figure 4.28. Nickel speciation at 5°C and 15°C for the three extraction methods; Ligands are grouped in categories: Organic = HA and FA; CO_3 = carbonatic ligands; OH = oxy-hydroxyl ligands.

During squeezing, as pH rises, there is an increase in Alkalinity (DIC) as well as DOC. These conditions are reflected in the speciation, where CO_3 (which here expresses all the possible carbonate ligands) and Cl play an important part in complexing Ni, as does HA and FA. As a consequence less

Ni^{2+} is available during those stages of the extraction, which is otherwise as much as 85-90% during the other two extractions and early squeezing.

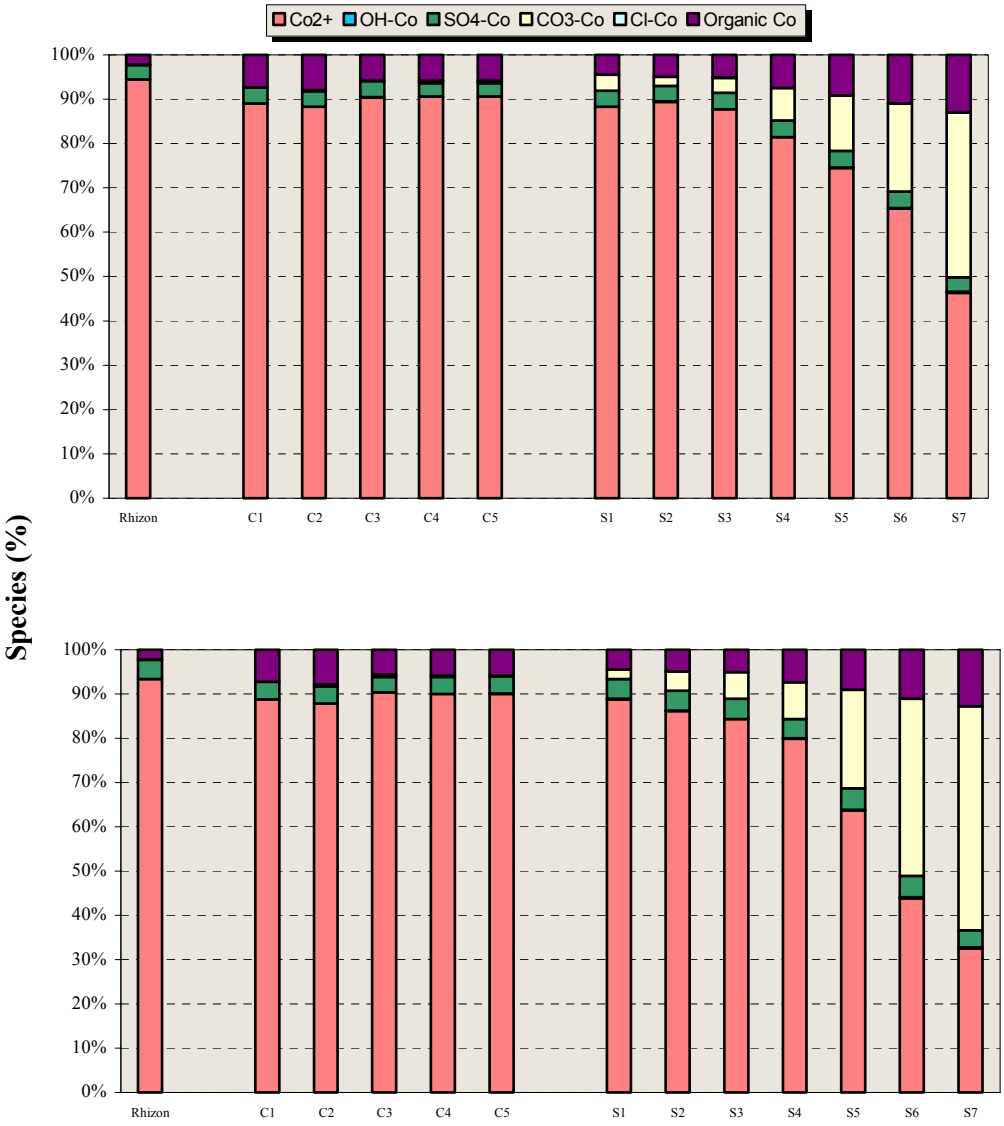


Figure 4.29. Cobalt speciation at 5°C and 15°C for the three extraction methods; Ligands are grouped in categories: Organic = HA and FA; CO_3 = carbonatic ligands; OH = oxy-hydroxyl ligands.

Similarly, Cobalt is mostly present as Co^{2+} but binds preferentially with CO_3 and alternatively with HA and FA (Fig. 4.29). However, an increase in solution concentration is also observed under the conditions of the progressive squeezing steps. There is evidence that Co, which associates

strongly with Fe and especially Mn oxides by chemisorption and co-precipitation, is strongly bound as Co^{3+} on Mn oxides under oxidizing conditions. As a consequence, as the pH rises and reducing conditions are established, Co could be released by the dissolution of Mn oxides as well as being increasingly complexed by HA and FA and CO_3 (up to 50% at 15°C). In this case the free ion and the total Co activities will diverge from one another, showing that speciation has changed and complexation has taken place (Fig. 4.30).

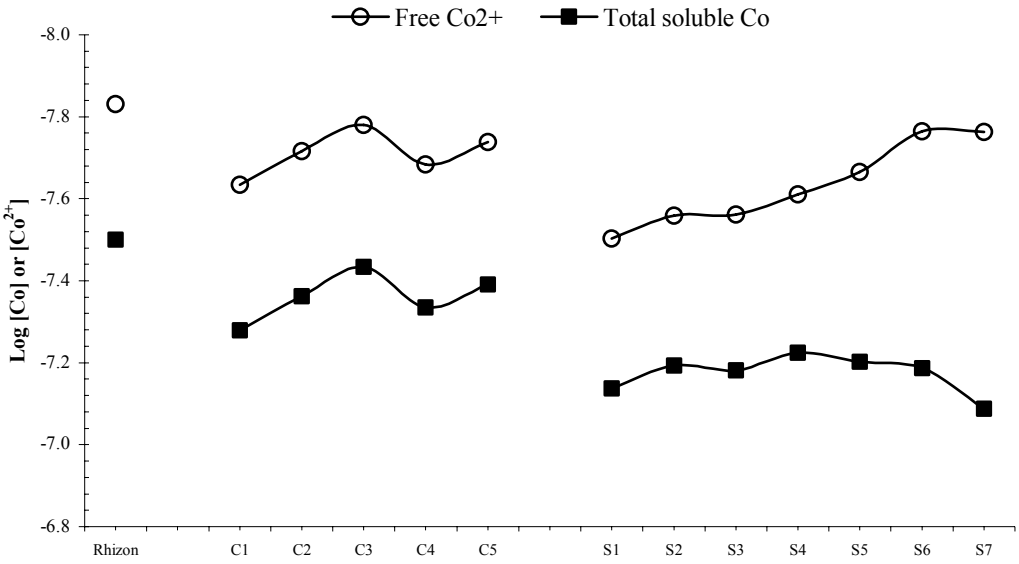


Figure 4.30. Total soluble and free ion Cobalt activities for pore water samples at at 15°C.

4.7.4.3. Copper, Chromium and Lead

Chromium, copper and lead are strongly bound to DOC in solution and speciation confirms this tendency, showing a percentage of complexed metal as high as 99%. However, these metals show different behaviour during the extractions. Cr and Cu present differences between the two temperatures: a steady or decreasing concentration for centrifugation at 5°C and a two-stage behaviour during the extractions at 15°C (see Fig. 4.31 and Fig. 4.32).

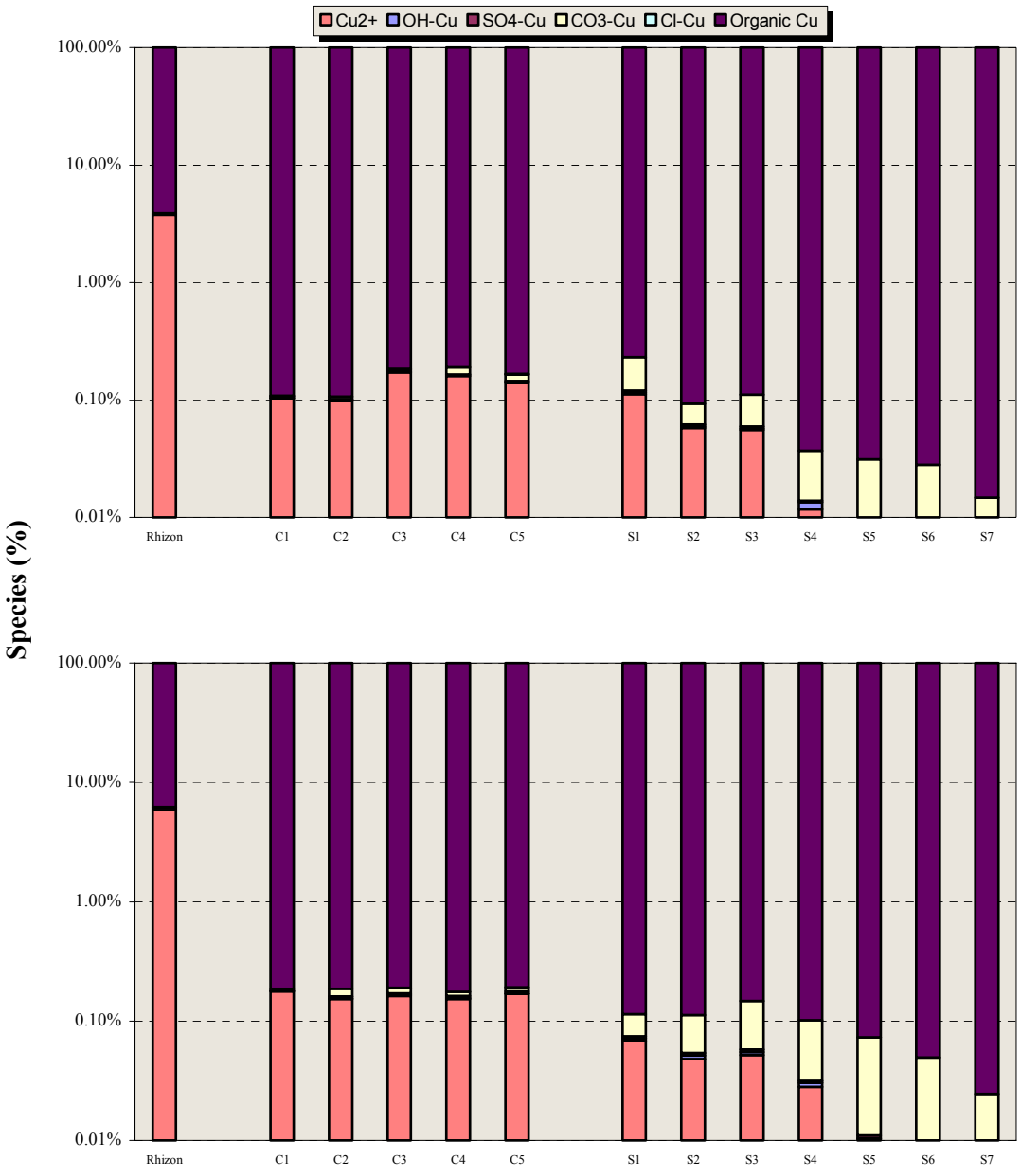


Figure 4.31. Copper speciation at 5°C and 15°C for the three extraction methods; Ligands are grouped in categories: Organic = HA and FA; CO_3 = carbonatic ligands; OH = oxy-hydroxyl ligands. Note logarithmic scale on Y-axis.

Cupric ions form complexes with many different ligands. In solutions above neutral pH the form $Cu(OH)_3^-$ may predominate. A strong $CuCO_3$ (aq) ion pair is also thought to be the major form in aerated natural water containing dissolved CO_2 species (Hem, 1989). However organic ligands are proven to

be the main bonding means for Cu (see Tipping, 2002; Baker and Senft, 1995) in many studies and pore waters extracted for this study confirm this evidence (Fig 4.31). Nevertheless, even though Cu was essentially bond only to humus and DOC rose during squeezing (see Fig. 4.6 – 4.17), Cu in solution decreased. A possible explanation is that an increase in adsorption on solid phase humus may over-ride the increase in DOC which ideally should increase Cu in solution. In fact, most of the colloidal materials of soils (oxides of Mn, Al, and Fe, silicate clays and humus) adsorb Cu^{2+} strongly, and increasingly so as the pH is raised (McBride, 1994). Furthermore, Cu has a much lower mobility in reducing conditions such as those occurring during the later stages of the squeezing extraction.

Results and speciation for Cr are presented in Fig. 4.32. Organically-bound Cr appears to dominate, although this may be an over-simplification due to the lack of more comprehensive thermodynamic data within the model adopted (only Cr(III) is considered). Cr concentrations were significantly greater during the early stages of centrifugation extraction compared to later and squeezed samples. This is a common observation for other elements (Pb, Cu at 15°C, Na, K, Sr, Ba, Mn, Co, Ni at 5°C, Zn, Al, Sb and DOC, see Fig. 4.6 – 4.17) and could be mirroring the concentration and solubility of DOC during the extraction. In general, chromium, as other oxyanion-forming elements (e.g. As, Sb, Se, Mo, V, U, Re), tends to become less strongly sorbed as the pH increases (Dzombak and Morel, 1990). Besides, Cr can be mobilized as stable Cr(VI) oxyanion species under oxidizing conditions, but forms cationic Cr(III) species in reducing environment and hence behaves like other trace cations (i.e. is relatively immobile at near-neutral pH values). Chromate is in pH-dependent equilibrium with the other forms of Cr(VI) such as $HCrO_4^-$ and dichromate ($Cr_2O_7^{2-}$) with CrO_4^{2-} the predominant form at pH > 6 (McGrath, 1995). Furthermore, Cr(VI) is a strongly oxidizing

species, and in the presence of soil organic matter is reduced to Cr(III) (Bartlett and James, 1988).

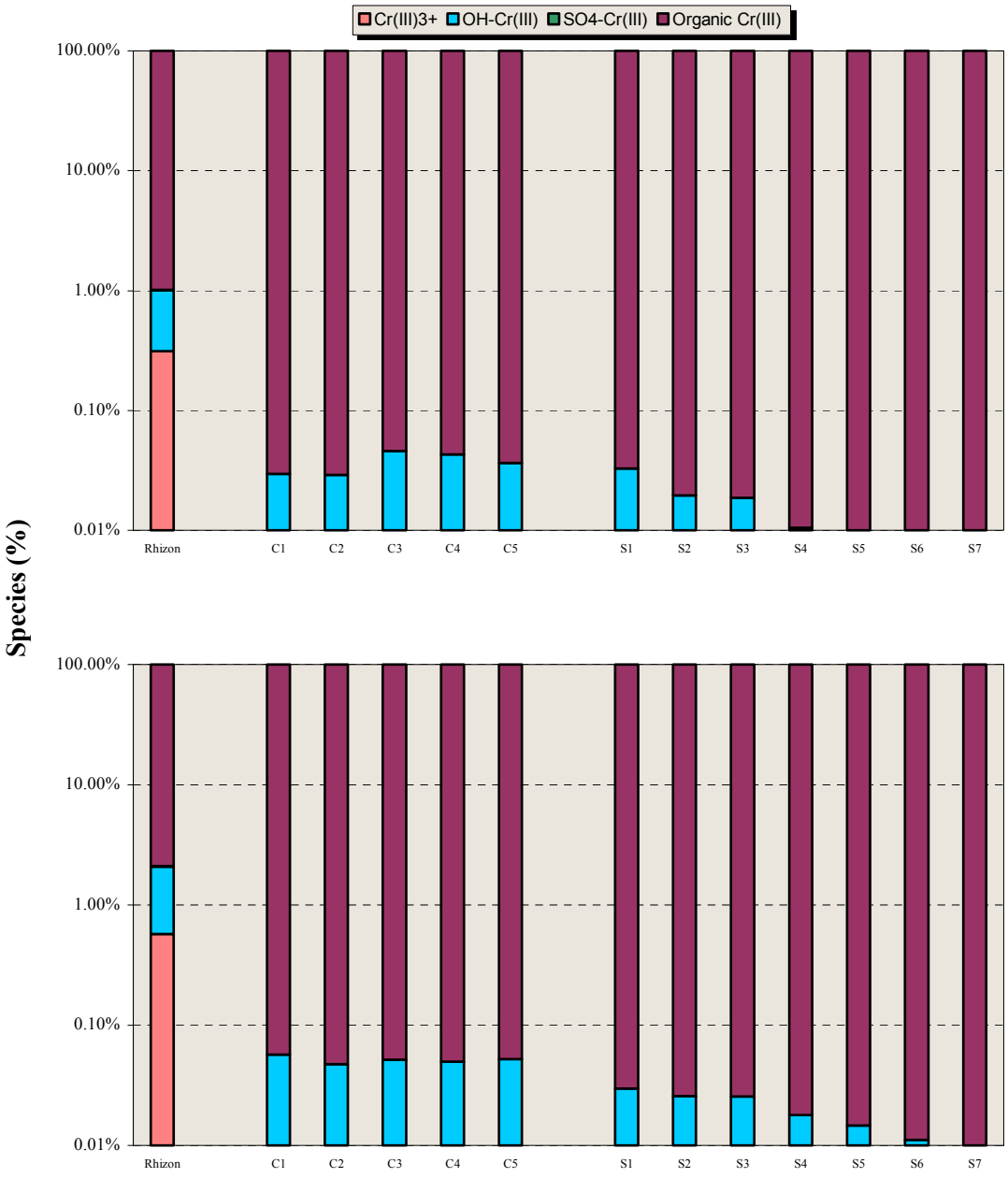


Figure 4.32. Chromium speciation at 5°C and 15°C for the three extraction methods; Ligands are grouped in categories: Organic = HA and FA; OH = oxy-hydroxyl ligands. Note logarithmic scale on Y-axis.

This reduction is common in the majority of soils, thus favouring the presence of the relatively insoluble and less mobile Cr(III) form, generally occurring as insoluble hydroxides and oxides (Grove and Ellis, 1980). Cr(III) in these forms complexes with organic acids (FA and soil extract of water-soluble organic matter), maintaining small amounts of Cr(III) in solution above the pH at which uncomplexed Cr precipitates and is therefore a means for enhancing its mobility (James and Bartlett, 1983). Bartlett and James (1983) also found that the amount of Cr(III) oxidized to Cr(VI) was proportional to the Mn reduced (and to the amount of reducible hydroquinone). This could be the reason why Cr concentrations at 15°C for squeezing extractions are mirroring those of Mn, reflecting Cr(VI) entering in solution, oxidised from the less mobile Cr(III).

Lead presents higher concentrations during centrifugation than during squeezing, where it even disappears from solution samples from S3 onwards at 15°C (see Fig. 4.12). Lead is the least mobile of the trace metals in soils and is particularly affected by reducing conditions. Higher pH and alkalinity promote Pb precipitation or co-precipitation as the carbonate, confirmed by the data of this study (Fig. 4.33), but also as hydroxide or phosphate. Furthermore, Pb^{2+} has high affinity for Mn oxide, which is thought to oxidise Pb^{2+} to Pb^{4+}, a very insoluble ion. Lead is also strongly chalcophilic and becomes very insoluble in reduced soils because of its precipitation by sulphide generated by sulphate reduction; however the redox potential calculated does not seem to suggest these conditions for the soil studied (i.e. sulphate reduction), although that cannot be ruled out completely at least as a minor co-reason.

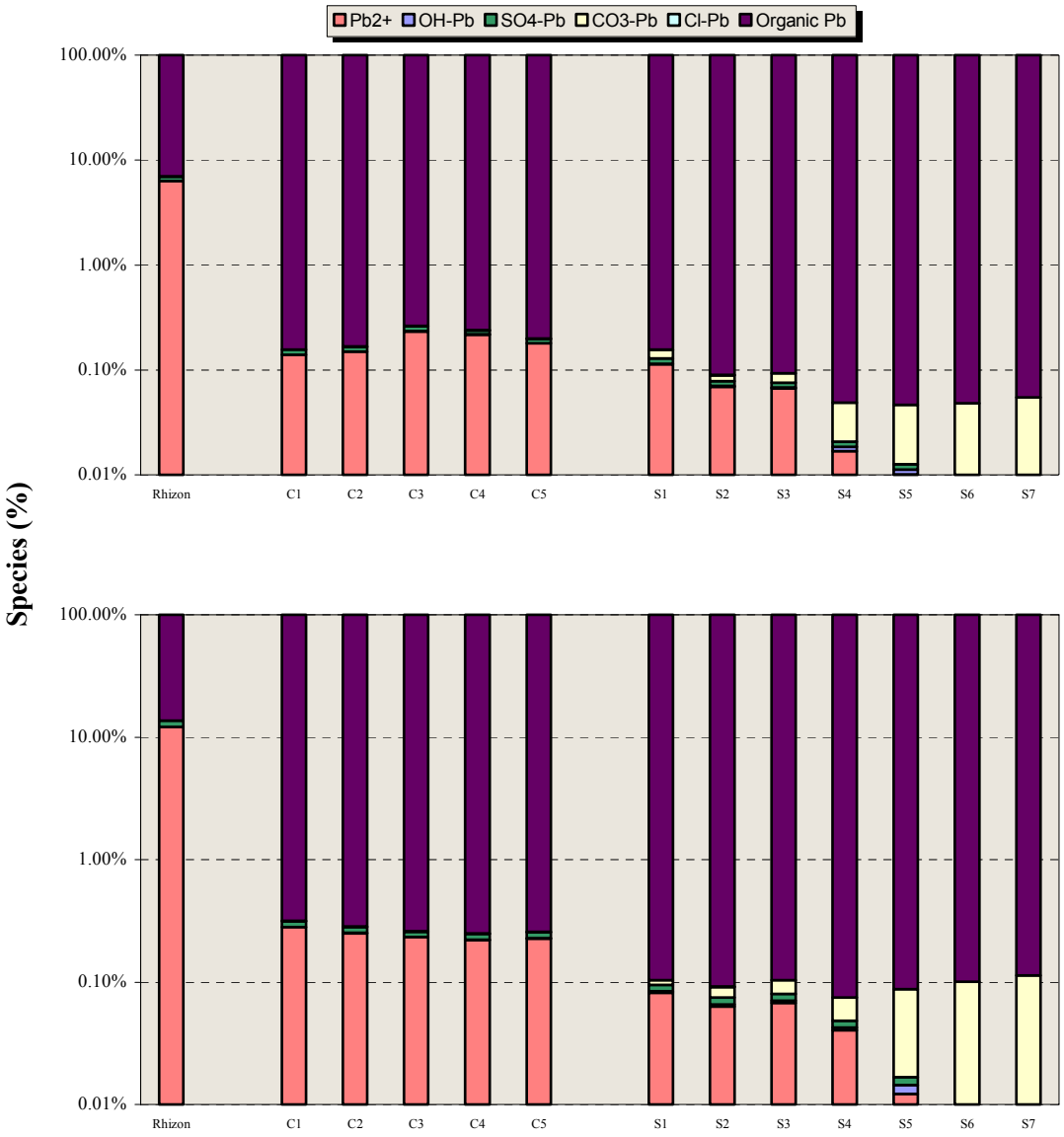


Figure 4.33. Lead speciation at 5°C and 15°C for the three extraction methods; Ligands are grouped in categories: Organic = HA and FA; CO_3 = carbonatic ligands; OH = oxy-hydroxyl ligands. Note logarithmic scale on the Y-axis.

4.7.4.4. Arsenic

The behaviour of As in solution is strongly dependant on its oxidation state, which in turn is affected by several factors with redox conditions playing an important part (Masscheleyed *et al.*, 1991). Therefore the increase

of As concentration observed during squeezing extraction could depend upon these conditions. As is not included in the WHAM-VI database, although it is present within the solution components that can be uploaded for a simulation. In other words it was not possible to model As speciation and its interaction with HA and FA, therefore speciation was carried out using PHREEQCi. Nevertheless, it is generally accepted that organo-arsenic complexes constitute a minor fraction of total dissolved As in soil pore waters (Sadiq, 1997). Organic forms of As are often linked to methylation reactions by microorganisms, which leads to the formation of several possible compounds (see O'Neill, 1995) and is linked to the supply of anthropogenic compounds (e.g., fertilizers and pesticides).

Using PHREEQCi for the speciation allowed the inclusion of Eh in the simulation. Results show that almost all As was present as As(V), despite the changing redox potential occurring during squeezing (Fig. 4.34). In general, arsenate (As(V)) and arsenite (As (III)) are the main forms of As in soils, with As(V) dominating (mainly oxyanions with various degrees of protonation) in aerobic soils, whereas As(III) predominate in slightly reduced soils, with increasing mobility under alkaline conditions. The pKa values indicate that H_3AsO_4 for As(III) and $H_2AsO_4^-$ and $HAsO_4^{2-}$ for As(V) are the predominant species at pH 2 to 9 (O'Neill, 1995). In slightly reducing conditions, both arsenate (As(V)) and arsenite (As(III)) can be released into solution by the dissolution of Fe and Mn oxides. Then the desorbed arsenate is reduced to arsenite, the most likely form to be found in these conditions. This is eventually converted to insoluble forms (McGeehan and Naylor, 1994), producing a two-stage As solubility, which first increases and then decreases if anaerobic conditions are maintained.

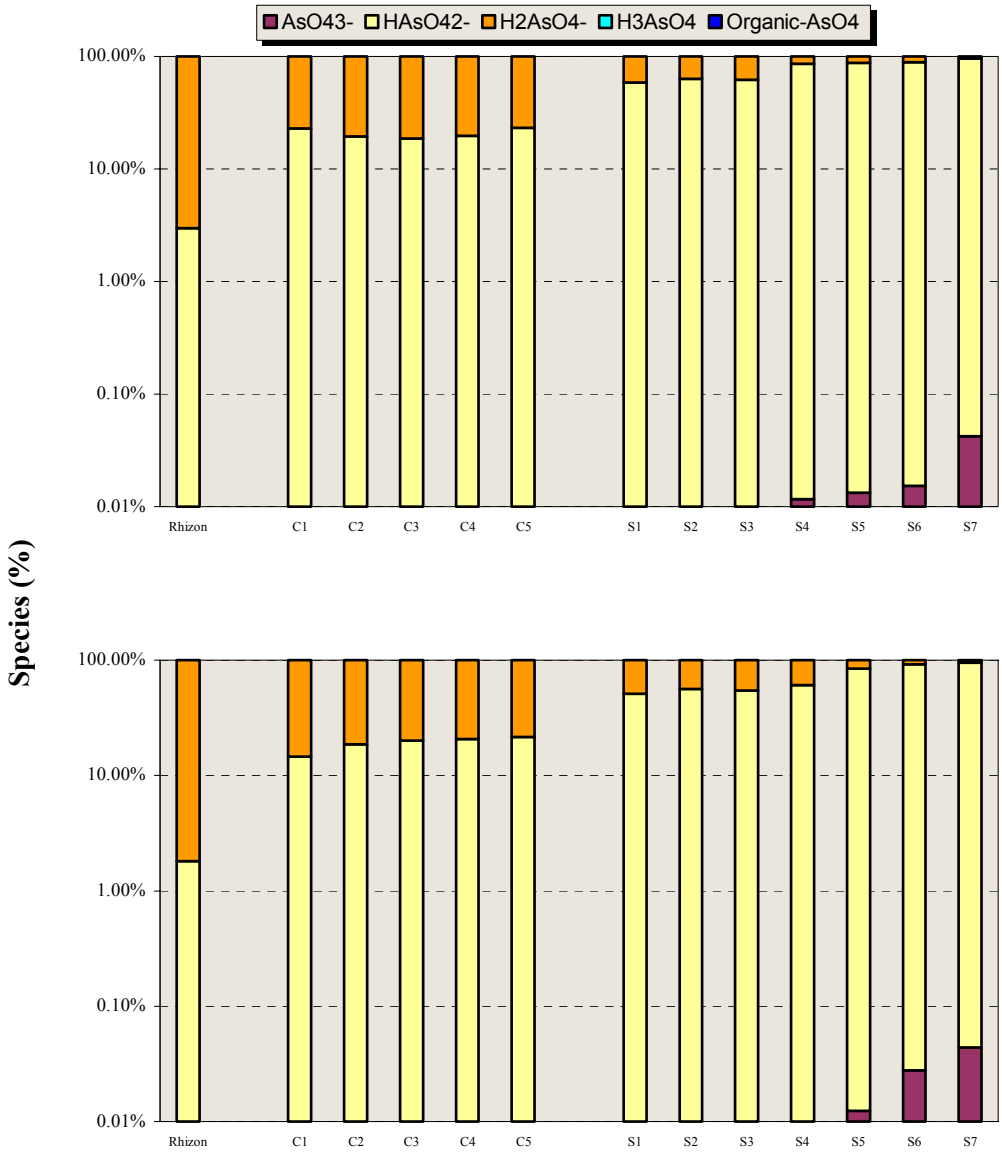


Figure 4.34. Arsenic speciation at 5°C and 15°C for the three extraction methods. Note logarithmic scale on Y-axis.

The results for this study do not seem to reach the second stage, where As solubility decreases again, but this could be due to other factors (Fig. 4.34). In fact, several competing processes can be involved when a soil remains in suboxic conditions for extended periods. For example, sulfides may form and

co-precipitate As in its lower oxidation state, a consequence of the chalcophilic tendencies of this element. Nevertheless, the increase in solution concentration and the speciation indicate that As could be affected by the change in redox conditions during squeezing, whereas its concentration does not show any variation during centrifugation extraction (see also Fig. 4.13).

The changes in oxidation states linked to the variation in pH and Eh have slow kinetics in an aqueous system, which explains why the species found in interstitial water do not always follow to the expected distribution (Onken and Hossner, 1996). McGeehan and Naylor (1994) show that rate of desorption and disappearance of H_3AsO_3 and $H_2AsO_4^-$ are slower in soil with higher adsorption capacity, suggesting that sorption processes may influence redox transformations of As oxyanions.

4.7.4.5. Antimony, Vanadium and Molybdenum

Antimony (Sb), vanadium (V) and molybdenum (Mo) show similar behaviour to As in the extracted pore waters: their concentrations all increase markedly during squeezing. Unfortunately these elements are not yet supported by the WHAM-VI database, therefore it is not possible to model their speciation and interaction with HA and FA.

For antimony, speciation was carried out using PHREEQCi. This suggests that $Sb(OH)_3$ is the main species in solution, matching almost perfectly the total Sb concentration in solution, while the other species are insignificant (Fig. 4.35). This clearly underestimates the complexity of Sb solution chemistry, which can occur either as antimonite (Sb(III)) and antimonate (Sb(V)), each being stable under reducing and oxidising conditions, respectively (McBride, 1994). In fact, equilibrium calculation alone does not seem suitable for the Sb biogeochemical cycle, since reduced species are found in oxic waters and vice versa, which point to a significant role played by kinetics. Antimony is classed as moderately mobile in soils (Kabata-

Pendias and Pendias, 1984), but mobility is thought to decrease under reducing conditions. In reducing soil pore waters, Sb^{3+} is likely to be in the form of the uncharged $Sb(OH)_3°$ molecule, whereas at very alkaline pH it converts into $Sb(OH)_4^-$. It is therefore likely that the increase in solution concentration observed during squeezing is due to antimonite (Sb(III)) entering in solution caused by mineral dissolution. In particular, hydrous oxides of Mn, Fe and Al are reported to specifically sorb antimony from dilute (µmol L^{-1}) $Sb(OH)_3$. The uptake capacity follows the sequence (Thanabalasingam and Pickering, 1990):

$$MnOOH > Al(OH)_3 > FeOOH$$

with the retention dropping rapidly at pH higher than 7. Belzile *et al*., (2001) also pointed out a mechanism by which antimonite can be adsorbed by Mn oxide with the release of Sb(V) and Mn(II). More recently, Chen *et al*., (2003) found a direct correlation between the profiles of dissolved Fe, Mn and inorganic Sb in pore waters from a freshwater lake, particularly in a relatively reducing environment, where peaks of dissolved Mn, sulfide and Sb(III) were present. Simultaneous increase of dissolved Fe, Mn and Sb were related to the dissolution of Fe and Mn oxyhydroxides under reducing conditions, with the concomitant release of the adsorbed Sb. The release of Mn in solution through reduction could therefore be invoked for part of the behaviour of Sb in the studied soil pore waters, showing a slight decrease during centrifugation and steadily increasing during squeezing. This further emphasises the different conditions during the two methods of extraction.

Complexes with humic substances are also possible (Crecelius *et al*., 1974; Pilarski *et al*., 1995), but are likely to be limited. In a recent review, Filella *et al*., (2002) exposed this lack of congruent studies on the element. They emphasise how few data exist on Sb(V) binding by low molecular weight organic ligands, whereas more extensive studies exist for Sb(III), which behaves as a borderline metal. Information on Sb interaction with OM is also

sparse and does not allow a conclusion to be drawn regarding its role in aquatic systems, but it seems to be minor.

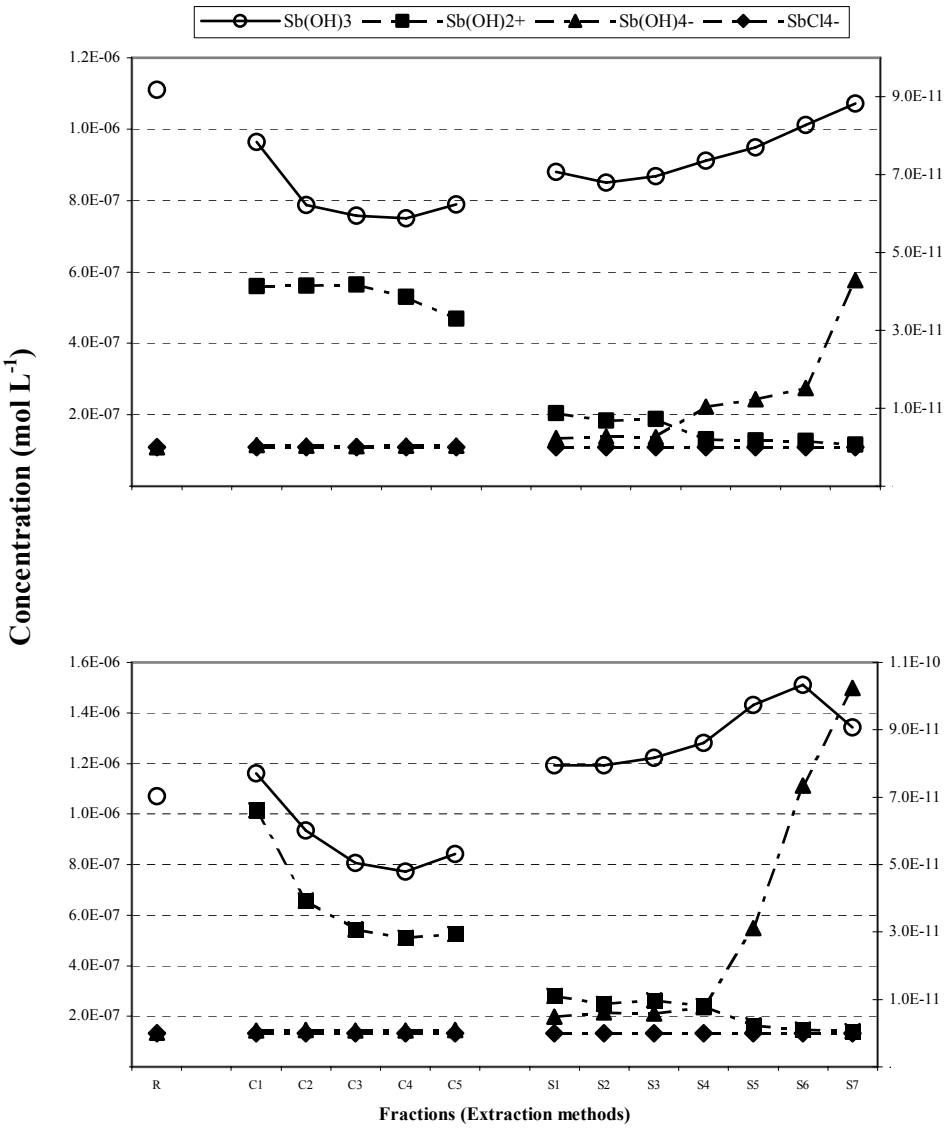


Figure 4.35. Antimony species at 5°C and 15°C as modeled by PHREEQCi, imposing the calculated Eh. $Sb(OH)_3$ refers to primary (left) axis; $Sb(OH)_2^+$, $Sb(OH)_4^-$ and $SbCl_4^-$ refere to the right axis; $HSb_2S_4^-$ and $Sb_2S_4^{2-}$ have been omitted because not significant.

In general, anionic elements such as Sb(V) in solution are less likely to interact with organic matter due to the predominantly negative charge of the natural organic compounds at natural pH, as pointed out by Pilarski *et al.*,

(1995). However, Chen *et al*., (2003) found that from 35-85% and from 35-55% of Sb in pore waters of two different lake sediment was present in a refractory fraction. This could be partially or entirely composed of organic matter which released free Sb into solution after UV treatment. These authors also observed an effect of sulfide in solution, with the formation of SbS_4^{3-} particularly favoured at pH values between 6 and 8. They concluded that several factors can affect Sb mobility in sediments and pore waters. Apart from its oxidation state and kinetics considerations, complexation with organic matter and sulfides seems to play an important role, as well as sorption onto Fe and Mn oxyhydroxides under oxidizing conditions (with release under reducing conditions), onto Fe sulfides under reducing conditions, which also implies a role of pH. In the studied soil, dissolved sulfides might not play such an important part in Sb solubility, which is likely to be strongly dependant on the redox status of the waters, and the presence of increasing amount of dissolved Sb (likely to be Sb(III)) can be taken as a direct effect of the more reducing conditions present.

Vanadium and molybdenum are also redox-sensitive elements, where their oxidation state as well as their solubility depends upon the redox conditions. V presents a rather complicated geochemistry, with three different oxidations states (III, IV and V) that are stable in aqueous solution, although it is likely that the dominant forms are V(V) anionic complexes with oxygen and hydroxide (Hem, 1989; McBride, 1994) occurring as vanadate ($VO_3(OH)^{2-}$, $VO_2(OH)_2^-$, $VO(OH)°_3$, and more complex polymeric anions) or as V (IV) vanadyl cations (VO^{2+}). Data suggest that oxidation state (V) is dominant but the (IV) state is equally important in the rhizon sample at 5°C (Fig. 4.36). This is confirmed by the increases in the $VO_3(OH)^{2-}$ and the higher proportions of the other vanadate species compared to the other two oxidation states.

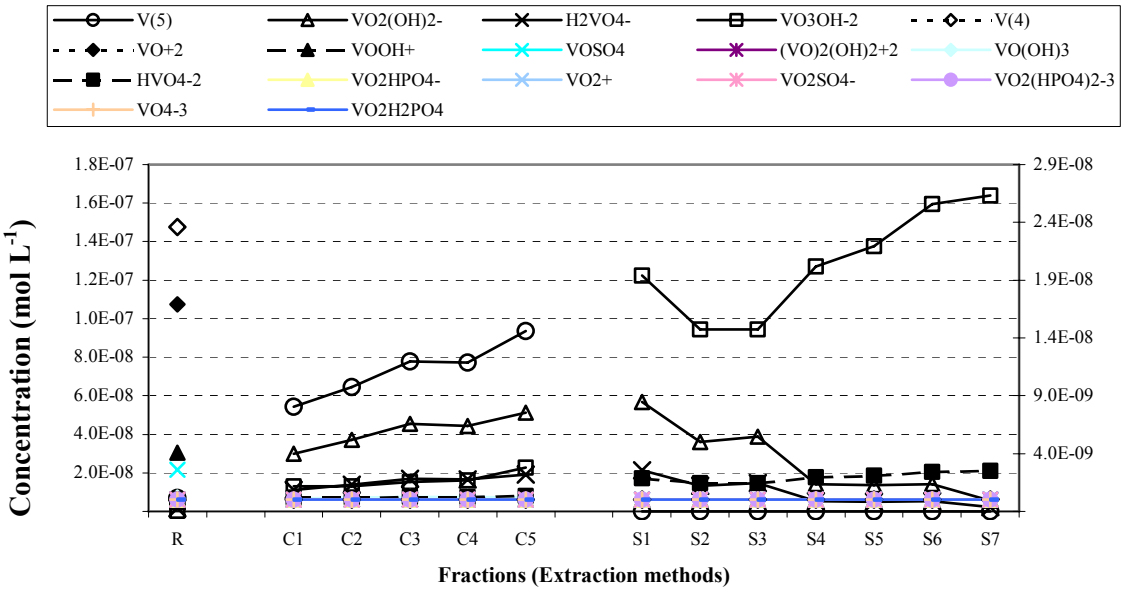


Figure 4.36. Vanadium species at 5°C as calculated by PHREEQCi. Full lines refer to principal Y-axis (left), dotted lines to secondary Y-axis (right).

Exchanges between these different V 'pools' that can be envisaged in a soils system (Fig 4.37) will depend upon prevailing physical, chemical and biological conditions (Alloway, 1995). Taylor and Giles (1970) suggested that V could move as a vanadyl complex in certain soils, especially when associated with Fe oxides. Vanadate anions adsorb to both Mn and Fe oxyhydroxides (Wehrli and Stumm, 1989) and bind on oxide and silicates most effectively at low pH, following the pattern of phosphate and other oxyanions. V can therefore be released into solution as Mn is reduced and remobilised (Morford and Emerson, 1999). Lower pHs or the absence of oxygen favour reduction of vanadate into vanadyl, which chemisorbs on oxides and aluminosilicates (clays) and complexes strongly with organic matter. Different authors (e.g., Templeton and Chasteen, 1980; Senesi, 1992) suggested that VO^{2+} tends to form stronger inner sphere complexes with O-containing ligands such as carboxylic and phenolic-OH (HA).

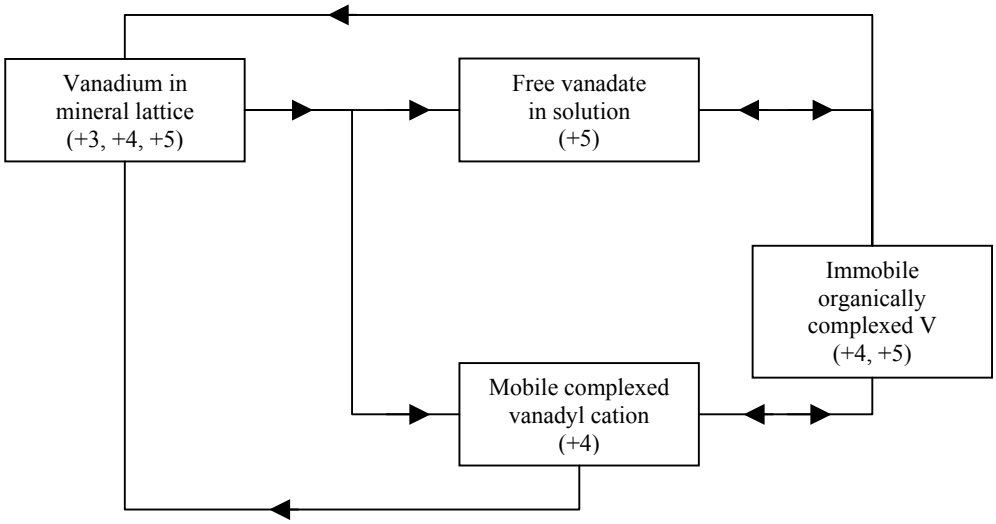


Figure 4.37. Vanadium pools in soil, after Edwards *et al.*, (1995).

Cheshire *et al*. (1977), showed association of V with humic and fulvic acid fractions of a soil, and compared this with other metals. Fulvic acid showed to be preferred by V and the percentage of total metals in a soil extracted by alkali (i.e. humic and fulvic acid fractions) decreased in the order:

Cu > Al > V > Ni = Co > Mn > Cr > Fe > Sr > Ba

As a general result, V solubility is in practice driven both by pH, being greater in alkaline and lower in acid conditions, and by redox conditions. Vanadium removal from pore waters is thought to occur below the level of either Mn or Fe oxyhydroxide reduction (Shaw *et al*., 1990, Kato *et al*., 1995; Hastings *et al*., 1996). Greater release of V into pore water for squeezed samples could be initially due to higher pH compared to centrifugation and squeezing, but changing redox and removal of Mn could then enhance this process, explaining the much greater concentrations as squeezing progresses, especially at 15° C. An increase in V concentration was also observed during centrifugation at 5° C, probably associated with minor pH and DIC variations. There may however be several simultaneous factors contributing

to V behaviour in the solid-water system, hence additional study is needed to understand these aspects.

For molybdenum, speciation was not possible either by WHAM-VI or PHREEQCi: the former does not include Mo in the database, the latter does not make provision of Mo species in solution, considering only MoO_4^{2-}. Molybdenum usually presents oxidation states between (III) and (VI) but Mo(IV) and Mo(VI) predominate under reducing and oxidizing conditions respectively (Alloway, 1995). Mo exists in solution mainly as molybdate anion, MoO_4^{2-}, which presumably can equally be considered the main species in the studied pore waters. Concentrations varied from 0.59 and 1.98 µg L^{-1} for the rhizon samples (at 5 and 15°C respectively) up to 19 and 48 µg L^{-1} for the last squeezing sample (at 5 and 15°C respectively) (see Fig. 4.11). The observed increase in Mo is consistent with MnO_2 reduction and increased pH. The higher Mn at the start of centrifugation is also mirrored by higher Mo. However rhizon samples showed much lower Mo concentrations, probably due to the same reasons which resulted in lower DOC concentrations with this extraction method.

Molybdate shows an increased solubility with increasing pH, due to hydroxyl ion competition for specific absorption sites. Mobilised anions are readily co-precipitated by organic matter and cations, or are adsorbed by sesquioxides. Studies of soil surface reactions have shown that molybdate is most strongly adsorbed with hydrous Fe and Al oxides (e.g. goethite, hematite). Molybdate ions tend to polymerise, and an extensive series of such species can exist, depending on pH and total Mo concentration (Mannheim, 1978), which has to be higher than 10 mg L^{-1}. There are also suggestions (Hem, 1989) that waters containing substantial concentrations of dissolved Ca^{2+} should not contain large concentrations of dissolved Mo, based on the solubility product for calcium molybdate ($10^{-8.7}$, Mannheim, 1978). On the other hand, organic complexation of Mo is not yet fully understood, and its

effect in soil may be obscured by pH or Eh as a consequence of poor drainage. In these conditions, soils have been found often to have high levels of available Mo, because of their high pH and organic status, which in turn favours the mobilisation of anions. Vlek and Lindsay (1977) proposed a simple equation to relate Mo availability to pH:

$$Soil + MoO_4^{2-} \rightarrow soil\text{-}MoO_4 + 2OH^-$$

Molybdenum is also thought to be released from organic matter with which it bonds probably in the same way as borate does (two adjacent OH groups, polyphenols). The possibility of organic matter enhancing Mo availability over a range of pH is increased by organic chelation of Mo preventing diagenesis (Mason and Berry, 1968).

In general Mo is indicated to have high geochemical mobility, a tendency to enter into solution in water under normal superficial conditions (Kaback, 1976), with anaerobic conditions resulting in the persistence of the anionic form (Gupta, 1971). All these observations seem to be confirmed by the data of this study, where Mo is released in pore waters at increasing concentrations, especially with increasing temperature and progressing squeezing.

4.8. Conclusions

From the comparison of the three methods studied for the extraction of soil pore water samples, it appears evident that differences exist between sample compositions under the conditions imposed. Rhizon samples, which represent a point-source method, are generally comparable with centrifugation samples, although often yield lower trace metal concentrations. This may have been due to the normal preparation of the used rhizon samplers, which have been shown in the previous chapter to be surface-coated with organic films, which modify their total porosity and, following acid washing, produce a protonated surface cation exchange capacity. Multiple-step methods (centrifugation and squeezing) clearly reveal

that the specimens are subjected to different conditions during extraction: an open system for centrifugation (i.e. gases – chiefly CO_2 – can be exchanged and are in equilibrium with atmosphere) and a closed system for squeezing. This in turn generates different, time-dependant chemical (and redox) conditions within the solid-solution system: increasing reduction and pCO_2 during the later stage of squeezing extraction are evident. This was shown especially by some of the main redox indicators such as NO_3^-, Mn and S, as well as the pH and alkalinity, which rose during squeezing but remained fairly constant during centrifugation.

Ionic strength generally decreased along the squeezing extraction gradient, in agreement with previous studies (Cave *et al*., 1998). Conversely, some elements appear to have a different behaviour, showing a marked increase during squeezing while being stable during centrifugation.

Following speciation, samples from centrifugation and the rhizon sampler showed a constant ratio of bioavailable species (free ion form) compared to the total solution concentrations, whereas squeezed samples exhibited considerable variability, with increasingly lower free ion species amounts from sample S1 to S7. This could be due to a combination of factors, either working synergistically or competitively;

- Lower total metal concentration of samples S5-6 and 7
- Decreasing ionic strength
- Lower moisture content (compared to centrifugation and rhizon)
- Increased adsorption of metals on solid phase due to modified solid-solution conditions
- Difference in the class of soil pore sampled (thinner films around particles, i.e. less available water)
- Mineral dissolution and precipitation
- Increasing total alkalinity
- Increasing pH
- Increasing reduction

- Temperature
- Incubation conditions
- Time

Further studies are clearly needed to clarify these points and to what extent they influence the pore water composition during its extraction from the soil. However, the most important factors seem to be controlled by the conditions during extraction. For equal incubation times and conditions, the time employed for the pore water extractions and the environment in which soil samples run into (open and closed systems), may or may not trigger different chemical conditions, testified by changes in pH, alkalinity, redox potential and ultimately adsorption conditions during squeezing. However, the increasing pressure applied and the progressive decrease in ionic strength as well as moisture content, do not rule out completely the possibility that less available water (thinner films around particles or intra-aggregate water) could be sampled during later stages of the squeezing extraction, therefore participating to the set of different conditions of the solid-solution system.

The methods employed for this experiment partially revealed their value as well as their flaws. Rhizon samplers showed to be subjected to modifications with time, involving a decrease in porosity and possibly implying significant variations in solute chemistry. In such cases, careful considerations should be given to the presence of humic substances in the soil, and on the conclusions drawn from such results. It follows that their best usage is probably as disposable samplers, which increases the experimental costs in the case of larger designs. They also present a limited window of moisture conditions in which to be used, resulting in reduced applications to field or dryer conditions. However, the fact that there is no equipment required except syringes (or vacuum tubes), together with their ease of handling/deployment and straightforward use certainly constitute

major advantages. Furthermore, if M^{2+} (free ion activity) were needed as opposed to M_{sol} (total metal in pore water), as often required in environmental studies, then Rhizon samplers present no 'side-effects'. Centrifugation presents fewer material problems, although tubes and other spare parts are not always commercially available (with few exceptions, e.g. www.ufaventures.com) and often have to be built in house. Chemical composition of pore waters extracted by this method was relatively reproducible, even with varying centrifugal speed. This suggests that the method is optimal for bulk solution studies, or when homogenisation represents a key experimental point. Targeted studies are also possible but would necessitate prior examination of the soil water holding capacity and release under varying centrifugal speeds, which could be time and effort demanding. Squeezing showed greater potentiality, giving the possibility to design bulk extraction (single, high pressure applied) or progressive 'quasi-equilibrium' extraction (numerous steps with equilibration time). However, limitations emerged in the case study of a long duration extraction, caused by reduction which produced marked changes in the pore water chemistry and speciation. In addition, the method is not as accessible as the other two, at least with the present apparatus required. In summary, the importance of the method employed for the soil pore water extraction should not be underestimated. Experiment design and performance should be chosen to reflect the particular aim of the study, and the parameter operationally defined as a function of the method employed.

5. Effect of soil:solution ratio on apparent trace metal buffer capacity

5.1. Introduction

5.1.1. Solubility, mobility and complexation of trace elements

Metals are present within the soil system in different 'pools'. For example, trace elements can be immobilized within the soil by adsorption and subsequent 'fixation'. Metal precipitates (and co-precipitates) of carbonates, phosphates, oxides etc. may be present at higher concentration of metals. On the other hand, soluble organic acids may form aqueous complexes with trace metals, facilitating transport to the lower mineral soil or to surface water. Therefore, the mineral soil may serve as a trace metal sink through adsorption and precipitation reactions or as a trace metal source through desorption and dissolution reactions (Evans, 1989; Selim and Sparks, 2001).
Metal adsorption/desorption and solubility studies are important in the characterization of metal mobility and availability in soils. The relationship between the soluble/mobile and immobile metal pools is a function of the physico-chemical characteristics of the metals, selected soil properties and environmental conditions.

Metal desorption/dissolution processes primarily depend on characteristics such as soil pH, redox potential, adsorption and exchange capacity, the ionic strength of soil pore water, competing ions, and kinetic effects (e.g. contact time) (Evans, 1989; McBride, 1994; Sparks, 1995; Impellitteri *et al*., 2001). Buffering of metal ions in solution can usefully be expressed in terms of a Quantity/Intensity (Q/I) relation. The 'Quantity' is represented by the amount of sorbed metal in rapid equilibrium with the soil pore water, i.e. the desorbable fraction, and the 'Intensity' is normally the activity of uncomplexed ions in the soil pore water.

5.1.2. Effect of pore water characteristics on metal desorption

Adsorption equilibria are often summarised by the *distribution or partition coefficient*, K_d, which expresses the relative affinity for a sorbate in solution to be absorbed or desorbed (Oscarson and Hume, 1998). The distribution coefficient, K_d, is usually defined as the ratio of concentrations in the adsorbed and liquid phase, thus:

$$K_d = \frac{[M_{soil}]}{[M_{solution}]} \qquad (5.1)$$

usually expressed in L kg^{-1}. However, when reporting K_d values for soils, it is very important that the definitions of $[M_{soil}]$ and $[M_{solution}]$ are given, identifying what form of metals is described. For example, for estimating immediately bioavailable metal in soil pore water, the free ion activity estimated by speciation programs can be used (Jopony and Young, 1994); conversely, if the study focuses on metal transportation to groundwater, it may be more appropriate (pragmatically) to include all species of metals in solution (Impellitteri *et al*., 2001).

The extent to which a chemical is adsorbed or desorbed can generally be rationalised within the frameworks of solution and surface chemistry. *Internal* and *external* factors affecting sorption and/or desorption can be distinguished (Harter and Naidu, 2001). Examples of the first category are:

- Ionic strength
- Cation, anion and organic ligands
- pH
- Total metal concentration

Examples of the second category are:

- Pressure
- Temperature

- Soil:solution ratio (***R***)
- Experiment technique and sample storage conditions

5.2. The effect of soil:solution ratios in desorption studies

The ratio of soil to solution or particle concentration (C_p), represents one of the least determined factors that can affect metal partitioning. Widely different soil:solution ratios (***R***, kg L^{-1}) have been used to investigate the adsorption and desorption behaviour of trace-metals ions by soils (Table 5.1.).

Variations in ***R*** have been found to influence the aqueous-phase chemistry of trace-metal ions, and thereby affect sorption and desorption processes (O'Conner and Connolly, 1980; Voice *et al*., 1983; Di Toro, 1985; Celorie, 1989). Generally, K_d values tend to decrease with increasing soil concentration (high ***R***), suggesting increased metal solubility. Grover and Hance (1970) suggested that this effect is predominantly caused by higher surface area exposure at high ***R***. Another explanation would be that there are simply more particles that pass through a given filter at higher solid concentrations. Therefore, more particles transporting bound metal are erroneously analysed as 'soluble' or desorbed metals in a supernatant, yielding lower K_d values (Voice and Weber, 1985; Van Benschoten *et al*., 1998). A third and more plausible explanation is that K_d increases as labile metal is depleted (stronger sites accessed) and so a small value of ***R*** (substantial depletion) will produce a greater K_d value.

Early studies on this topic revealed that total concentrations of soluble salts generally decreased with an increase in the soil moisture content (increasing dilution) (Reitemeier, 1946, Khasawneh and Adams, 1967, Larsen and Widdowson, 1968).

Table 5.1. Some example of the background electrolyte composition and soil:solution ratios used in the literature, ordered by decreasing soil:solution ratio.

Trace metals	***R*** **kg L^{-1}**	Background electrolyte	Ionic strength mmol L^{-1}	Reference
Cr	1:1; 1:20	$NaNO_3$	100	Zachara *et al*. (1989)
Cd, Cu	1:4	$CaCl_2$	15-150	Petruzzelli *et al*. (1985)
Cd	1:10	$(Ca,Na)(Cl,NO_3)$	30	Boekhold *et al*. (1993)
Zn	1:10	$CaCl_2$, $Na(Cl,NO_3,SO_4)$	5-300	Elrashidi and O'Connor (1982)
Cu, Zn	1:10	$Mg(NO_3)_2$	10	Cernik *et al*. (1994)
Cd	1:20	$NaNO_3$, $Ca(NO_3)_2$	30	Naidu *et al*. (1994a, 1994b)
Cd, Cr, Cu, Ni, Pb, Zn	1:30	Na-acetate	10	Gao *et al*. (1998)
Cd	1:40	H_2O	-	Sanchez-Martin and Sanchez-Camazano (1993)
Cd	1:40	$Ca(NO_3)_2$	10	Gray *et al*. (1999)
Co, Cu, Ni	1:100	$CaCl_2$	0.5	Harter (1992)
Cu, Ni, Pb, Zn	1:100	H_2O	-	Harter (1983)
Cu	1:200	$Ca(NO_3)_2$	30	Atanassova and Okazaki (1997)

Source: Harter and Naidu, 2001 (modified).

From this point of view, the literature shows considerable agreement concerning the limited *buffer capacity* (or *buffer power*) of soil, i.e. solution concentrations of metals are not maintained at the same values with increasing dilution. Desorption seems to be strongly affected by change in ***R***, as demonstrated in the work of Fotovat and co-workers (1997), where, for 8 soils, there was a decrease in the cations concentrations, except for Ca, with decreasing ***R***. Changes in soil:solution ratio (***R*** from 3.3 to 0.2) affected the desorption characteristics of trace metals Cu and Zn, although the magnitude of the decrease was much greater for Cu (from 0.37 μmol_c L^{-1} to 0.161 μmol_c L^{-1}). The total concentration of DOC also decreased with ***R***, from 118 mg L^{-1} to 20.4 mg L^{-1} across the range of suspension densities used (Fotovat *et al*., 1997). Bordas and Bourg (2001) found that Pb, Cu, Zn and Cd were decreasingly remobilised from a fluvial sediment as the suspended solid concentrations were decreased; when the values of ***R*** was changed from 50 to 0.1 g L^{-1} (increasing dilution), the solubilized fraction of metals was reduced

by 96% for Cu, 77% for Pb, 99% for Zn and almost 100% for Cd compared to the initial concentrations. This would be expected if the buffer capacity of the sediment were incapable of providing complete replenishment to the solution phase. Similarly, Arsenic solubility has been shown to increase with ***R*** (Tan and Teo, 1987). You *et al*. (1999) employed six soil:solution ratios (***R*** from 50 to 0.8) to study the partitioning of organic matter (OM) in soil and expressed this in terms of a K_d value by determining the concentration of the native soluble OM. The results showed that an increase in ***R*** resulted in a smaller K_d value, i.e. in increasing solubility. More recently Yin *et al*. (2002) used a series of ***R*** values (from 0.5 to 0.02) in batch experiments to quantify the solubility of Cu, Ni and Zn in soils. Again, greater concentrations arose from larger values of ***R***.

5.2.1. Electrolyte solution and ionic strength

In addition to the variability in soil:solution ratio, the background electrolyte solution and ionic strength also vary widely between reported studies. It is commonplace in many soil and environmental studies to utilise 5 mmol L^{-1} (0.01 *N*) Ca^{2+} solutions (where the counter ion is NO_3^-, Cl^-, or occasionally, SO_4^{2-}) for batch equilibration with soil to mimic soil pore water ionic strength and composition (Wolt, 1994). This arises from a historical precedent originating from earlier studies of soil exchangeable cations and dissolved salt content, but is still largely used in many studies (Table 5.1). However, depending on the value of ***R***, the equilibrating solution may reflect the ionic strength and ion composition of the added electrolyte more than it does that of the *in situ* pore water. Some studies have not made provision for background electrolyte composition that would be comparable to the pore water, sometimes even having an ionic strength (*I*) that approaches zero (Table 5.1.). However, it is well known that solid⇌solution equilibria in soils depend significantly on ionic strength (*I*).

5.2.3. Objectives

In this chapter, the Stoke Bardolph soil was used in a batch experiment to investigate soil metal buffer capacity and metal desorption at different soil:solution ratio (***R*** values), characterizing the soil in terms of Quantity/ Intensity (Q/I) relationships. The soil:solution ratios were supposed to be the only variable and so particular care was taken to produce a background electrolyte solution that closely emulated the pore water composition and ionic strength found following extraction at FC using centrifugation. In addition, the experiment was intended to test the validity of utilizing equilibrated suspensions of soil as a means of characterizing metal ion activity and speciation in the soil pore water.

5.3. Materials and methods

5.3.1. Soil sampling and preparation

Soil sampling and preparation of the Stoke Bardolph soil was as previously described (see section 2.5.1.). Soil pore water was extracted by centrifugation from soil equilibrated at FC and incubated at two temperatures (5°C and 15°C) as described in section 4.6.2.2.

5.3.2. Batch experiment

An electrolyte solution was prepared, based on the composition of pore water from the Stoke Bardolph soil (Table 5.2). Only major anions and cations were considered in the make up of the synthetic soil pore water.

Six soil:solution ratios (***R***) were chosen: 1:100, 1:50, 1:25, 1:10, 1:5, 1:2 (see table 5.3.). Soil slurries were then prepared from the soil stored at two different temperatures (5°C and 15°C at FC). An appropriate mass of soil was added to a known volume of synthetic solution (Table 5.3) in order to achieve the correct range of soil:solution ratios. All soil suspensions were prepared in 100 mL centrifuge tubes except the 1:2 ratio, which was prepared in 250 mL

tubes in order to obtain enough supernatant solution for subsequent analyses; all batches were prepared in triplicate.

Table 5.2. Composition of the original pore water extracted from Stoke Bardolph soil equilibrated at 5° C and 15° C for and summary of the synthetic electrolyte preparation.

	Cl mg L^{-1}	NO_3 mg L^{-1}	SO_4 mg L^{-1}	Ca mg L^{-1}	Mg mg L^{-1}	K mg L^{-1}	Na mg L^{-1}	Ionic strength M
SB Centrifuge 5°C	11.2	1360	104	437	30.7	50.9	21.4	8.06E-02
SB Centrifuge 15°C	13.4	1968	142	597	38.0	71.2	26.1	1.14E-01
			ICP-AES control					
Background 5°C			107.3	495	31.9	44.5	20.5	
Background 15°C			152.5	623	38.4	60.1	24.3	

Background electrolyte 5°C		**Background electrolyte 15°C**	
Salts used	**mg L^{-1}**	Salts used	**mg L^{-1}**
KNO_3	132	**KNO_3**	184
$NaNO_3$	78.9	**$NaNO_3$**	96.6
$Mg(NO_3)_2.6H_2O$	323	**$Mg(NO_3)_2.6H_2O$**	400
$CaCl_2.2H_2O$	46.4	**$CaCl_2.2H_2O$**	27.7
$CaSO_4$	147	**$CaSO_4$**	202
$Ca(NO_3)_2.4H_2O$	2409	**$Ca(NO_3)_2.4H_2O$**	3121
Excess of N	**27.5**	**Excess of N**	**10.8**

Table 5.3. Soil:solution ratios and details of the mass balances for the preparation of slurries.

Ratio	R	θ_{fc}	$Soil_d$	$Soil_w$	H_2O soil	H_2O tube	H_2O final	Final soil suspensions
	g mL^{-1}		g	g	mL	mL	mL	g
1:100	0.01	0.52	0.36	0.55	0.19	35.8	36.0	36.4
1:50	0.02	0.52	0.72	1.10	0.38	35.6	36.0	36.7
1:25	0.04	0.52	1.40	2.13	0.73	35.3	36.0	37.4
1:10	0.1	0.52	3.60	5.48	1.88	34.1	36.0	39.6
1:5	0.2	0.52	7.20	11.0	3.77	32.2	36.0	43.2
1:2	0.5	0.52	18.0	27.4	9.42	26.6	36.0	54.0

θ_{fc} = water content at FC; **$Soil_d$** = dry soil; **$Soil_w$** = moist soil; ratios in g mL^{-1} are equivalent to kg L^{-1} (see data discussion and data normalization)

The soil suspensions were initially shaken on a reciprocal shaker at 5°C and 15 °C in two different controlled temperature rooms. A 24 h extraction time is generally typical for many batch extractions (e.g., Anderson and Christensen, 1988; Yin *et al*., 2002) but it may also vary and extend into several weeks according to the aim of the study (Jopony and Young, 1994). For this study, the shaking/equilibration time was chosen in accordance to previous desorption Q/I relationships studies (Raven and Hossner, 1994; Lee and Doolittle, 2002) and was set at 100 strokes min^{-1} for 72 h. The longer equilibration time was also selected to try to take into account the slow kinetics of the organic-metal desorption. The suspensions were then centrifuged at 3000 rpm for 1h or as necessary to separate a clear supernatant. The pH was measured on triplicate supernatants and on the remaining slurries. The supernatants were filtered using disposable 0.45 µm acrodiscs and kept in bottles and treated for analysis as previously described in this study (30 ml for DOC and DIC analysis, 15 ml acidified 1% v/v with HNO_3 for AAS and ICP-MS).

Bicarbonate (HCO_3^-) was measured using Gran plot titration. DIC and DOC were measured using a Shimadzu TOC-CPH total organic analyser fitted with an ASI-V autosampler. Flame AAS was used to measure Cu and Zn concentrations, whereas Al, Cr, Mn, Co, Ni, (Cu, Zn), As, Mo, Cd and Pb concentrations were measured by ICP-MS.

5.3.4. Chemical speciation

The total dissolved metal and ligand species in pore water and extracts were calculated using the WHAM-VI model (Tipping, 1998) as described in section 4.6.5.

5.4. Results and discussion

Results for the batch experiment are summarised in Table 5.4: total metal concentrations, total, organic and inorganic C, alkalinity and pH are given

for different soil:solution ratios (***R***) and two equilibration temperatures used. Although dilution of the major constituents of the pore water does not occur (i.e., the background electrolyte is always the same and *I* can be considered constant), for simplicity the term 'dilution' will be used for decreasing ***R***, referring to the suspended solid concentration.

Increasing dilution of the solid phase, generally produced a decrease in the concentration of soil-derived constituents in solution, in agreement with expectation and the findings of Fotovat *et al*. (1997); Al, Cr, Mn and Pb, were released in greater amounts at ***R*** = 0.5 (the lowest dilution, soil:solution ratio = 1:2), but otherwise they all decreased following the general pattern. A reason for this could be due to difficulties in separating the particulate fraction at higher ***R*** values, where a portion of the metals analysed might be ascribed to particulate or colloidal material (despite filtration), increasing the apparent solution concentration. This could be an effect of shaking the suspensions during the batch extractions at high ***R***, which may contribute to the amount of small particles due to particle-particle interaction and abrasion (the "solid effect" described by Sparks, 1995). The effect of reducing ***R*** was very marked on the concentrations of Zn and Ni, but was evident on the whole set of trace element analysed and appeared more pronounced at 15°C. There were generally greater concentrations at 15° C, in agreement with the general thermodynamic dependence of equilibrium solubility products on the temperature (e.g. Aharoni and Ungarish, 1977; Scheckel and Sparks, 2001). An increase in temperature tends to shift the equilibrium in favour of dissolution (Barrow, 1986).

Table 5.4. Total metal concentrations, solution pH, alkalinity and dissolved (organic and inorganic) carbon in pore waters and soil extracts for Stoke Bardolph soil incubated at FC and at two temperature (5° C and 15° C) for 4 weeks.

R‡		pH*	Al	Cr	Mn	Co	Ni	Cu	Zn	As	Mo	Cd	Pb	Total C	DIC	DOC	Alkalinity
g mL^{-1}			µmol L^{-1}											mg L^{-1}			mgC L^{-1}
Incubation at 5°C																	
FC†	2	6.28	1.031	0.456	0.780	0.081	26.66	2.759	29.32	0.409	0.078	0.091	0.017	125.46	1.50	124.0	
1:2	0.5	6.860	17.17	3.657	0.576	0.055	18.76	5.072	21.14	0.389	0.078	0.172	0.217	148.0	10.63	137.4	8.82
1:5	0.2	6.733	1.094	0.246	0.067	0.035	13.37	2.473	12.33	0.290	0.051	0.108	0.011	44.83	6.470	38.36	3.16
1:10	0.1	6.503	0.320	0.125	0.052	0.028	10.87	1.659	10.29	0.214	0.038	0.092	0.006	27.99	5.747	22.25	1.78
1:25	0.04	6.550	0.252	0.093	0.060	0.025	7.891	1.024	7.551	0.149	0.026	0.084	0.008	19.64	5.353	14.28	1.61
1:50	0.02	6.593	0.258	0.053	0.043	0.023	6.878	0.652	7.355	0.106	0.019	0.084	0.004	14.30	5.375	8.92	1.55
1:100	0.01	6.523	0.085	0.042	0.045	0.023	5.683	0.466	6.295	0.084	0.014	0.064	0.003	11.46	5.288	6.17	1.35
Incubation at 15°C																	
FC†	2	6.00	0.834	0.355	0.478	0.053	17.75	3.832	17.67	0.454	0.095	0.120	0.018	121.6	0.10	121.5	
1:2	0.5	7.053	13.028	3.081	5.874	0.082	19.91	5.542	26.56	0.457	0.094	0.210	0.180	182.6	13.40	169.2	14.82
1:5	0.2	6.990	1.594	0.483	0.619	0.047	17.12	3.189	18.76	0.356	0.065	0.153	0.027	53.65	9.157	44.50	6.36
1:10	0.1	6.975	1.444	0.409	0.146	0.038	13.88	2.450	14.98	0.285	0.059	0.131	0.024	40.57	8.611	31.96	5.03
1:25	0.04	6.743	0.696	0.186	0.068	0.032	10.37	1.329	10.74	0.180	0.046	0.108	0.011	24.55	7.805	16.75	3.26
1:50	0.02	6.740	0.451	0.118	0.049	0.029	8.005	0.893	7.786	0.124	0.033	0.097	0.007	16.78	6.617	10.16	2.81
1:100	0.01	6.733	0.285	0.077	0.047	0.029	6.063	0.602	6.164	0.090	0.022	0.084	0.004	13.00	6.600	6.400	2.22

†Values for pore water samples extracted by centrifugation at FC; ‡ Soil:solution ratios; * solution pH.

5.4.1. DOC release and solubility

Both DIC and DOC also decreased with increasing dilution; the effect was particularly pronounced for dissolved organic carbon (DOC). This degree of change was unexpected, especially given the high content of organic matter in the soil (27% LOI). However, these results are in agreement with those of You *et al*. (1999) and Yin *et al*. (2002) who found that increasing ***R*** produced an increase in organic carbon solubility. The variation in DOC with $\boldsymbol{R}^{-1}$ is shown in Fig. 5.1. Remarkably, it appears that the soil has virtually no capacity to buffer DOC, since the measured concentrations corresponded almost identically to the theoretical 'zero buffer capacity' trend, calculated relative to the DOC value found for the first value of ***R*** employed (***R*** = 0.5).

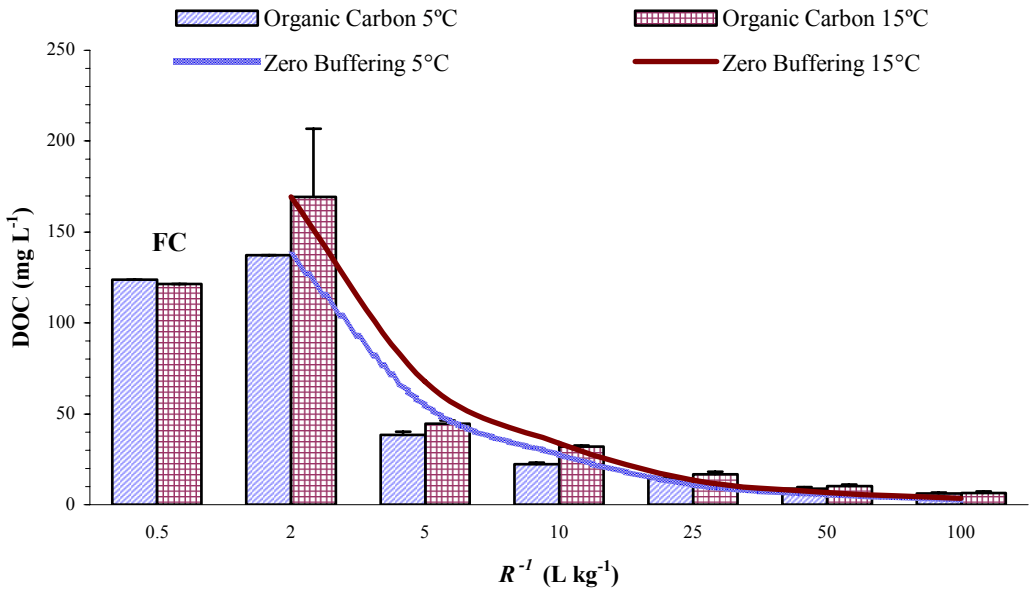


Figure 5.1. Effect of dilution on the concentration of dissolved organic matter in the soil suspensions equilibrated at 5°C and 15°C; dilution increases from left to right; lines represent hypothetical zero buffer capacity, calculated on the basis of the value of ***R*** employed; values at FC are for pore water extracted by centrifugation as in section 4.6.2.2.

It has been suggested that DOC may behave similarly to sparingly soluble salts following the solubility product principle (Fotovat *et al*., 1997), but if this

were the case then DOC would not vary so much with ***R***. The solubility of OM depends on the properties of the macromolecules that comprise humic substances (polyelectrolytes), (Hayes, 1985). Results seems rather to suggest that, despite a very large humus content, desorption of DOC is subject to marked hysteresis, therefore producing a lower DOC than that found in suspensions with larger values of ***R***. The bonding mechanisms of humic and fulvic acids (see Sposito, 1984 for a detailed description) could probably envisage this behaviour, as these macromolecules, with their multiple attachment sites, are strongly held to soil mineral surfaces.

Numerous studies have shown that time is an important factor for the desorption of organic compounds from soil and that the desorption may be so slow that sorption appears irreversible (Gu *et al*., 1994). Reemtsma and co-workers (1999) extended their soil column release experiment to longer timescales (5 d) in order to account for this problem. These authors observed two distinct phases of OM release (though not clearly separated from each other): an initial rapid, spontaneous desorption and a later phase of slow, diffusion-controlled desorption. They also suggest that the initial peak of desorption might be ascribed to the instantaneous release of organic substances held in the pore water or sorbed to external surfaces of the soil, from where they interchanged rapidly with the percolating aqueous phase, whereas the second phase is controlled by the transport of the organic material from the interior of the particulate phase towards the soil-water boundary. The length of shaking/equilibrating time imposed during the present experiment (3 d) seemed enough to allow the release of OM in solution even at low values of ***R***, but results are not conclusive in this sense.
Furthermore, the discrepancy between the DOC concentration in the pore water extracted by centrifugation at FC and the first ***R*** employed in the soil suspensions (***R*** = 0.5), could be partially explained by higher dispersion present in the latter, where solid particles were colliding or interacting in the 'slurry' of the batch extraction. This "solid effect" (or particle concentration

effect) has been documented elsewhere (e.g. Di Toro *et al*., 1986, Voice *et al*., 1983). Emerson (1959) described the theory of soil migroaggregates ("soil crumbs"), where units of colloidal clay, or domains, and coarser particles of silt and sand (quartz) are cemented together by humus, with polysaccharides playing a major role in their formation and stabilization (Harris *et al*., 1966). The aggregation (A) and dispersion (D) of these microaggreagates has been described as a reversible process and can be represented as follows (Bremmer, 1968):

$$\left[(C-P-OM)_x\right]_y \underset{A}{\overset{D}{\Leftrightarrow}} y(C-P-OM)_x \underset{A}{\overset{D}{\Leftrightarrow}} xy(C-P-OM) \qquad (5.2.)$$

where C indicates mineral particles (clay, etc.), P the polyvalent metal ion (Ca^{2+}, Mg^{2+}, Fe^{3+}, Al^{3+}, etc.), OM the humified organic matter, and C—P—OM the microaggregate consisting of mineral and organic colloids linked together through polyvalent cations. Migroaggregates will break down releasing cations and dissolved OM as the soil particles are dispersed by water shaking, and this effect may be more pronounced with increasing solid concentration. Therefore, increasing values of ***R*** may favour dispersion of these microaggregates resulting in more surfaces exposed and to a greater release of DOC in solution compared to the conditions for the extractions at FC.

In brief, data analysis reveals that there is a clear trend in DOC decreasing concentrations which follows the ***R*** values, as shown in Fig. 5.1 and confirmed by recent studies (You *et al*., 1999; Yin *et al*., 2002). The use of soil suspension could therefore be carried out assuming a nul buffer capacity to simply predict the concentrations of DOC at FC from higher dilutions. However, this observation needs to be corroborated by more robust and comprehensive studies (e.g. to account for different textures and soil compositions).

5.4.2. Metal solubility and speciation

Figure 5.2 to 5.6 show metal speciation for varying ***R*** and two temperatures employed. Decreasing ***R*** affected metal speciation. The relatively higher concentration of organic colloids at lower suspension dilutions contributes to higher soluble metal concentrations. Yin *et al*. (2002) suggested that, as the amount of water per mass of solids changes, there are also changes in the distribution of other ions such as Ca and Al. In general, with increasing dilution, free hydrated ions were sufficiently dissolved to maintain nearly constant concentrations and released into solution (buffering capacity), whereas the total concentration of metal in solution is proportionally reduced with ***R*** because the buffer capacity for DOC is apparently negligible. This caused a relative increase in the proportion of free hydrated ion activity in the speciation of the pore waters (Fig. 5.2, 5.3 and 5.4).

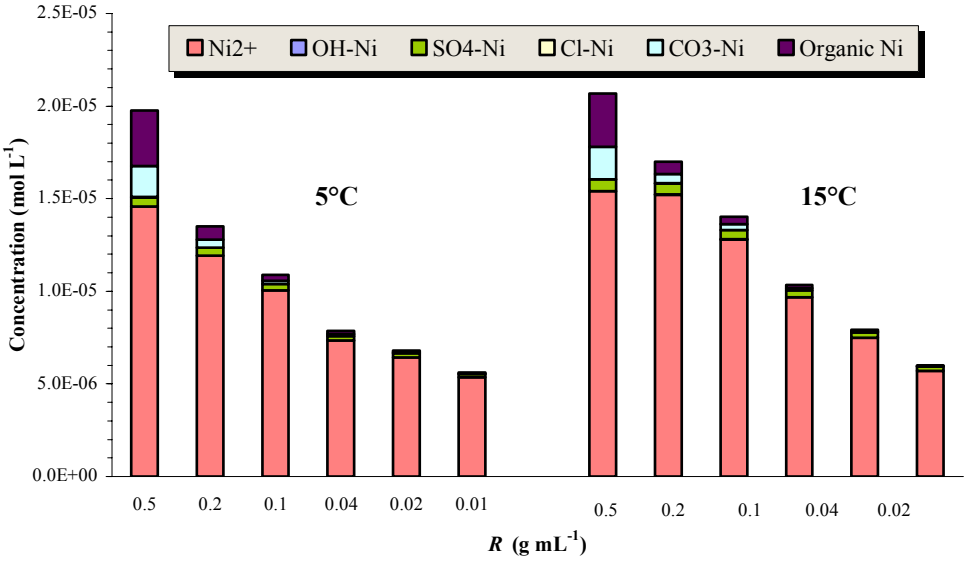


Figure 5.2. Speciation of Ni at two temperatures compared to varying soil:solution ratios; columns represent total solution concentrations of specified types of chemical species.

This effect is very apparent for Cu and Pb (Fig. 5.5 and 5.6), which are usually strongly complexed by humic and fulvic acids. Cd, Ni and Zn also show a net decrease in the proportion of complexed metal in favour of the free hydrated ion (Table 5.5).

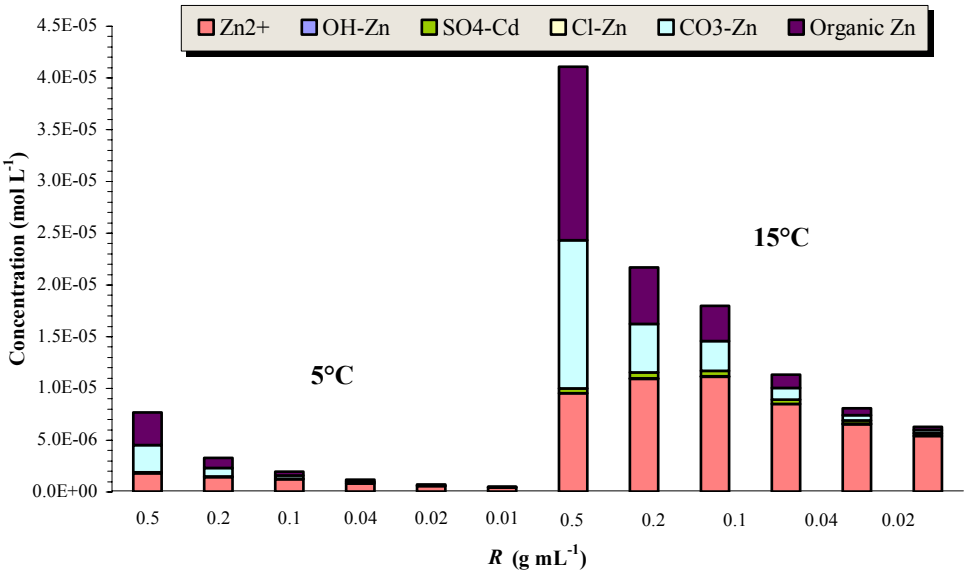


Figure 5.3. Speciation of Zn at two temperatures compared to varying soil:solution ratios; columns represent total solution concentrations of specified types of chemical species.

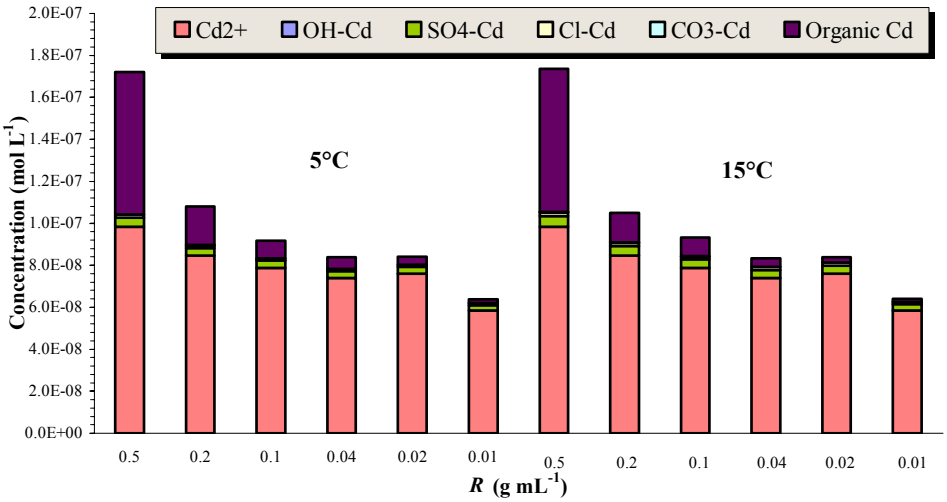


Figure 5.4. Speciation of Cd at two temperatures compared to varying soil:solution ratios; columns represent total solution concentrations of specified types of chemical species.

Table 5.5. Net percent increase in free ion concentration compared to the total solution concentrations; **Δ** represents the difference between ***R*** (1:100) and (1:2).

	$\Delta(Ni^{2+}/Ni_{sol})$	$\Delta(Zn^{2+}/Zn_{sol})$	$\Delta(Cd^{2+}/Cd_{sol})$	$\Delta(Cu^{2+}/Cu_{sol})$	$\Delta(Pb^{2+}/Pb_{sol})$
			%		
5°C	16.60	51.91	34.50	1.439	1.536
15°C	17.02	54.89	35.08	2.543	2.505

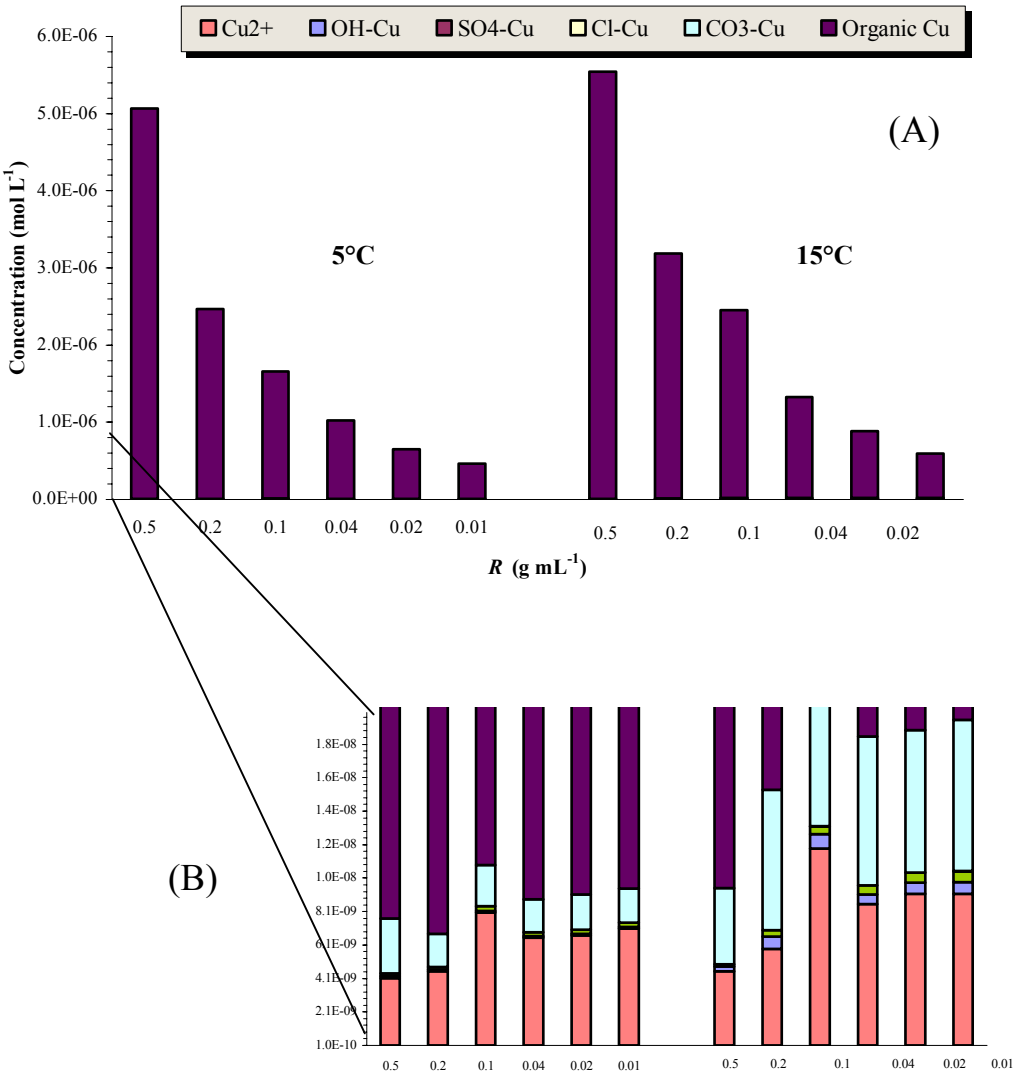


Figure 5.5. (A) Speciation of Cu at two temperatures compared to varying soil:solution ratios; columns represent total solution concentrations of specified types of chemical species; plot (B) shows the remaining ligands occurring at smaller concentrations.

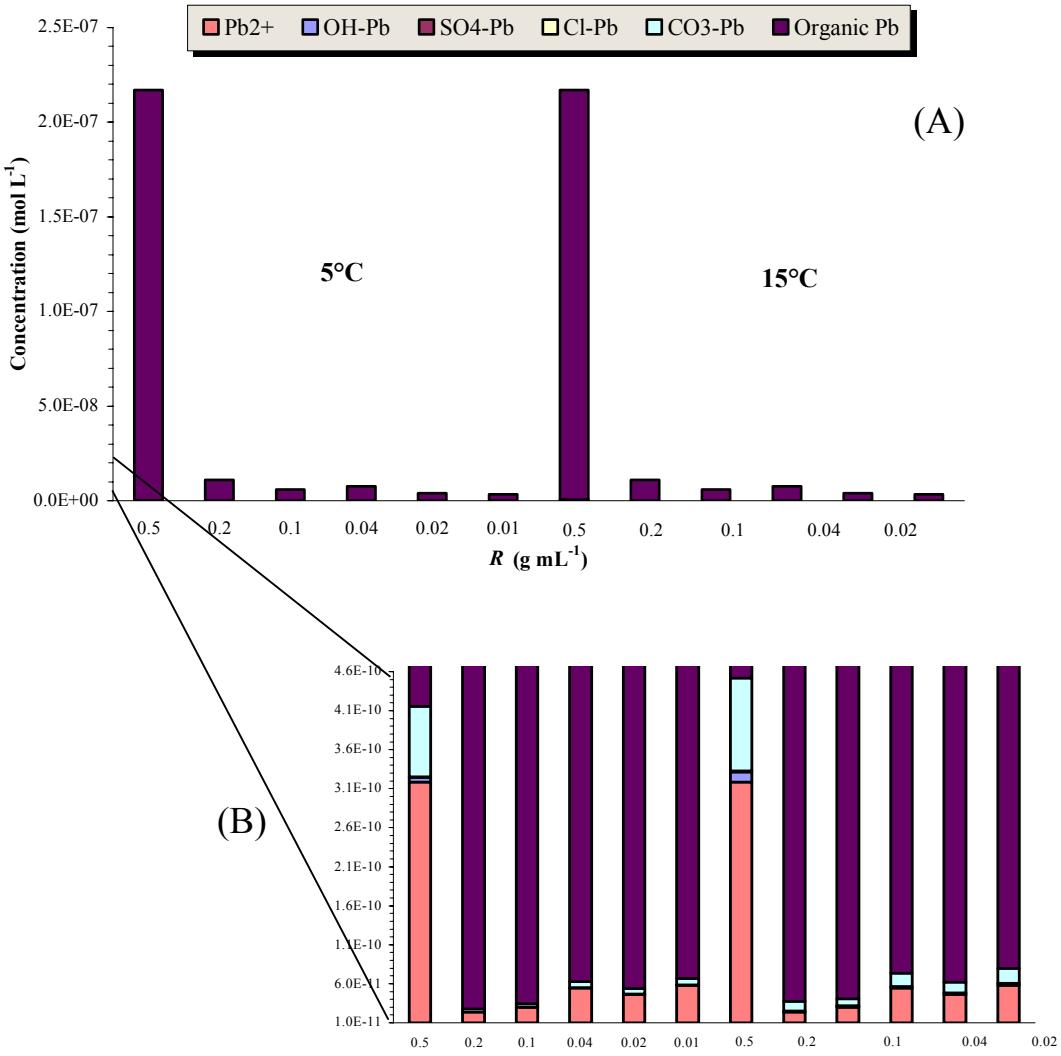


Figure 5.6. (A) Speciation of Pb at two temperatures compared to varying soil:solution ratios; columns represent total solution concentrations of specified types of chemical species; plot (B) shows the remaining ligands occurring at smaller concentrations.

These observations suggest that the soil's buffer capacity is sufficient to maintain fairly constant M^{2+} activity in the face of decreasing values of ***R***. (Fig 5.7), but there is only a very limited capacity to maintain DOC concentration.

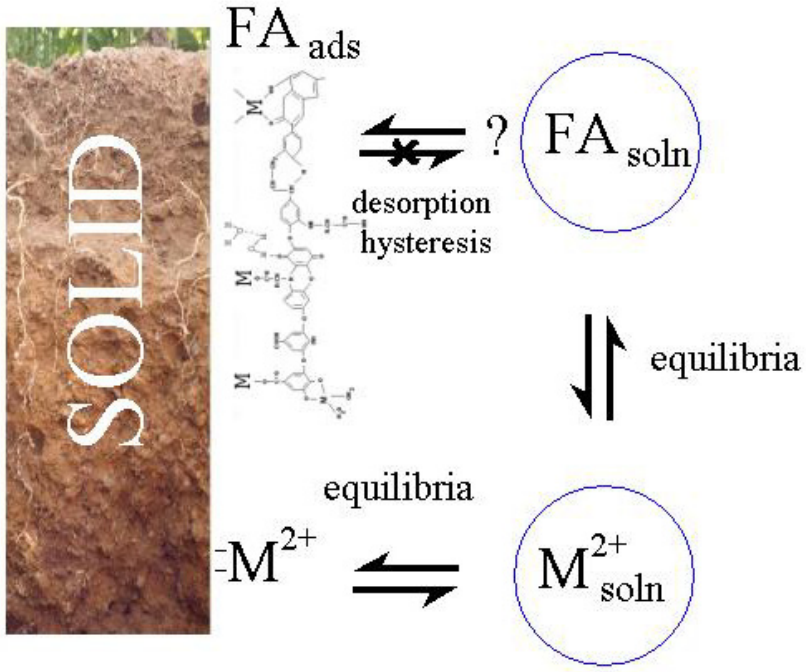


Figure 5.7. Schematic representation of the release of metals (M^{2+}) and humic matter (FA) in solution with increasing dilution, showing the possible desorption hysetresis happening in the case of humic substances strongly bond to the solid phase.

5.4.3. Metal ion buffering capacity

Given an infinite *buffer capacity*, the soil would maintain free metal ion activities at a constant level in response to decreasing ***R***. Apparently, this happens only partially, with each metal behaving differently. Figures 5.8 to 5.12 show measured values of free metal ion activity with varying ***R***, compared to a hypothetical 'infinite' and 'zero' free ion buffer capacity, as well as showing the corresponding total metal concentration. Total concentrations of M_{soln} appeared to depend strongly upon ***R***: Ni, Cd and, to a lesser degree, Zn at 15°C, appeared significantly close to the ideal infinite buffer power (linear) behaviour, but more generally the measured values showed an intermediate behaviour between the infinite and the zero buffer capacity. This was especially true for those metals which are highly complexed, such as Cu and Pb. Conversely, the behaviour of the free ion

concentrations seemed to be less dependent on ***R***: for example, $[Ni^{2+}]$, $[Cd^{2+}]$ and $[Zn^{2+}]$ at 15°C were almost invariant with increasing dilution, showing a very close match with the hypothetical 'infinite buffer capacity'. $[Cu^{2+}]$ and $[Pb^{2+}]$ showed more irregular behaviour with varying ***R***. For $[Cu^{2+}]$ it seems evident that, excluding the first value (***R*** = 0.5), which was taken as reference point, the concentration of free hydrated ion appeared to be buffered rather efficiently by the soil. As described earlier, the greater DOC concentration at ***R*** = 0.5 compared to the remaining (and decreasing) ***R***, affected the speciation and so the proportion of Cu^{2+} in solution. $[Pb^{2+}]$ concentrations, in addition to what just described, might have been influenced by the total $[Pb_{soln}]$, which appeared poorly buffered and irregularly distributed over the set of ***R*** and the two temperatures. Nevertheless, $[Pb^{2+}]$ at 15°C do not depart too significantly from the 'infinite buffer capacity'.

The kinetics of metal release (dissolution/desorption) could be different at different values of ***R***, perhaps accessing different labile metal pools. However, it is more likely that changes induced in the physico-chemical processes between the solid and the liquid phases of the soil during dilution may have contributed to the observed decrease in concentrations. The large polarisable Pb^{2+} cation is expected to be preferentially complexed by soft binding sites (e.g. S-, P-, and N-containing ligands). Humic substances and biota exudates and cell walls, contain a heterogeneous range of binding site types, some of which (minor sites) are soft donors and may thus be expected to play a role in complexation (buffering) of Pb (Town and Filella, 2002).

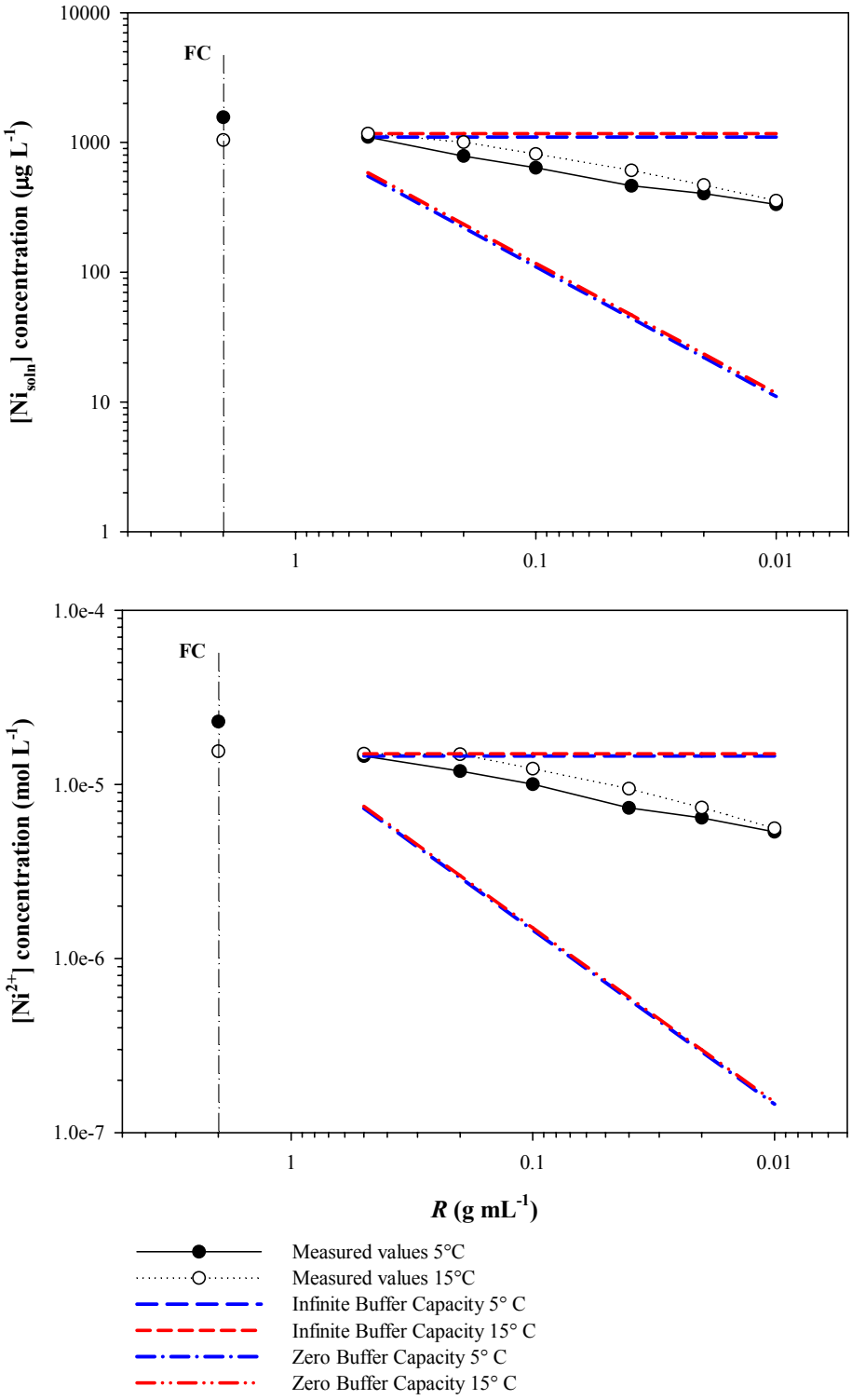


Figure 5.8. Total Ni and Ni^{2+} concentrations with varying soil:solution ratios compared to hypothetical 'infinite' or 'zero' buffer power.

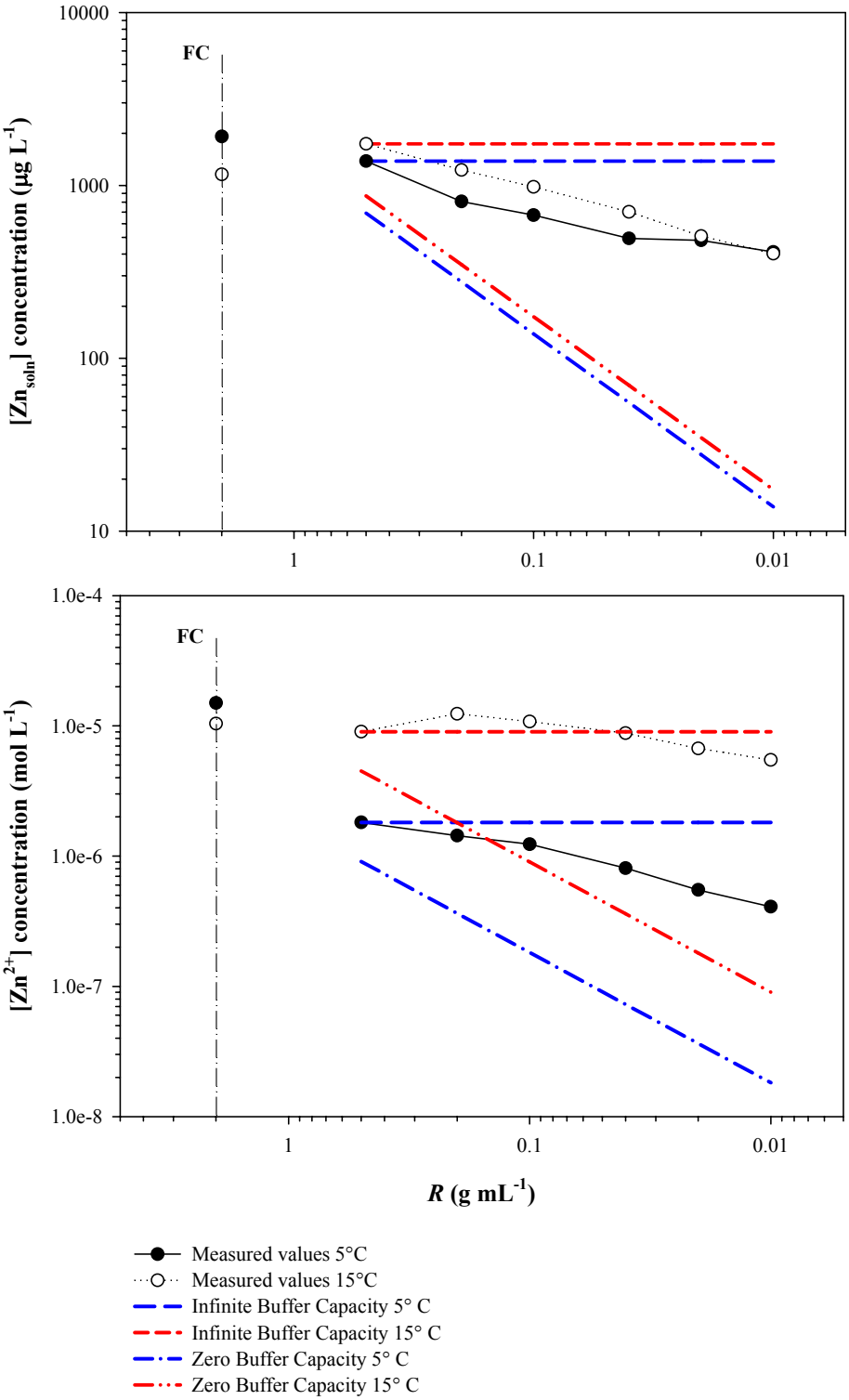


Figure 5.9. Total Zn and Zn^{2+} concentrations with varying soil:solution ratios compared to hypothetical 'infinite' or 'zero' buffer power.

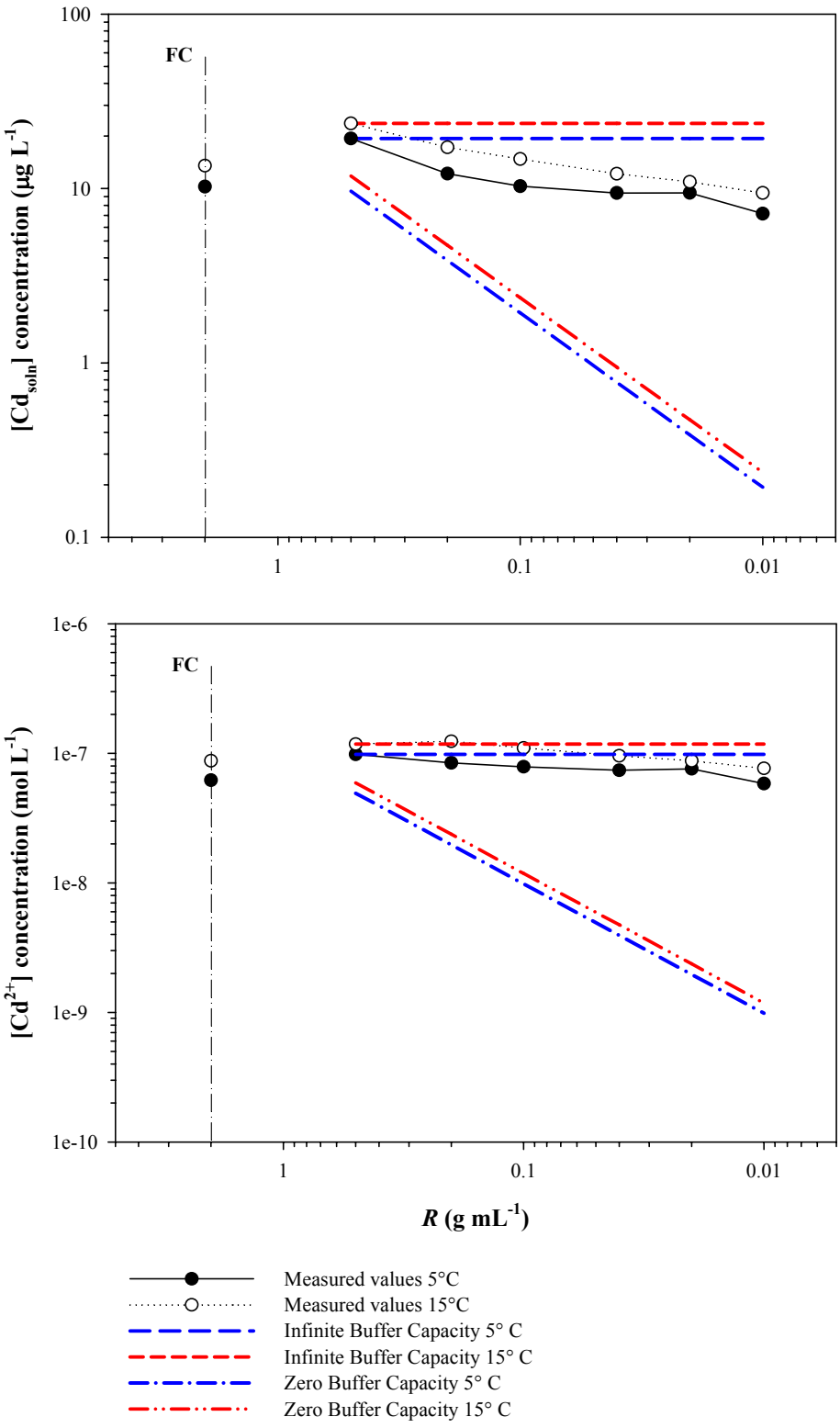


Figure 5.10. Total Cd and Cd^{2+} concentrations with varying soil:solution ratios compared to hypothetical 'infinite' or 'zero' buffer power.

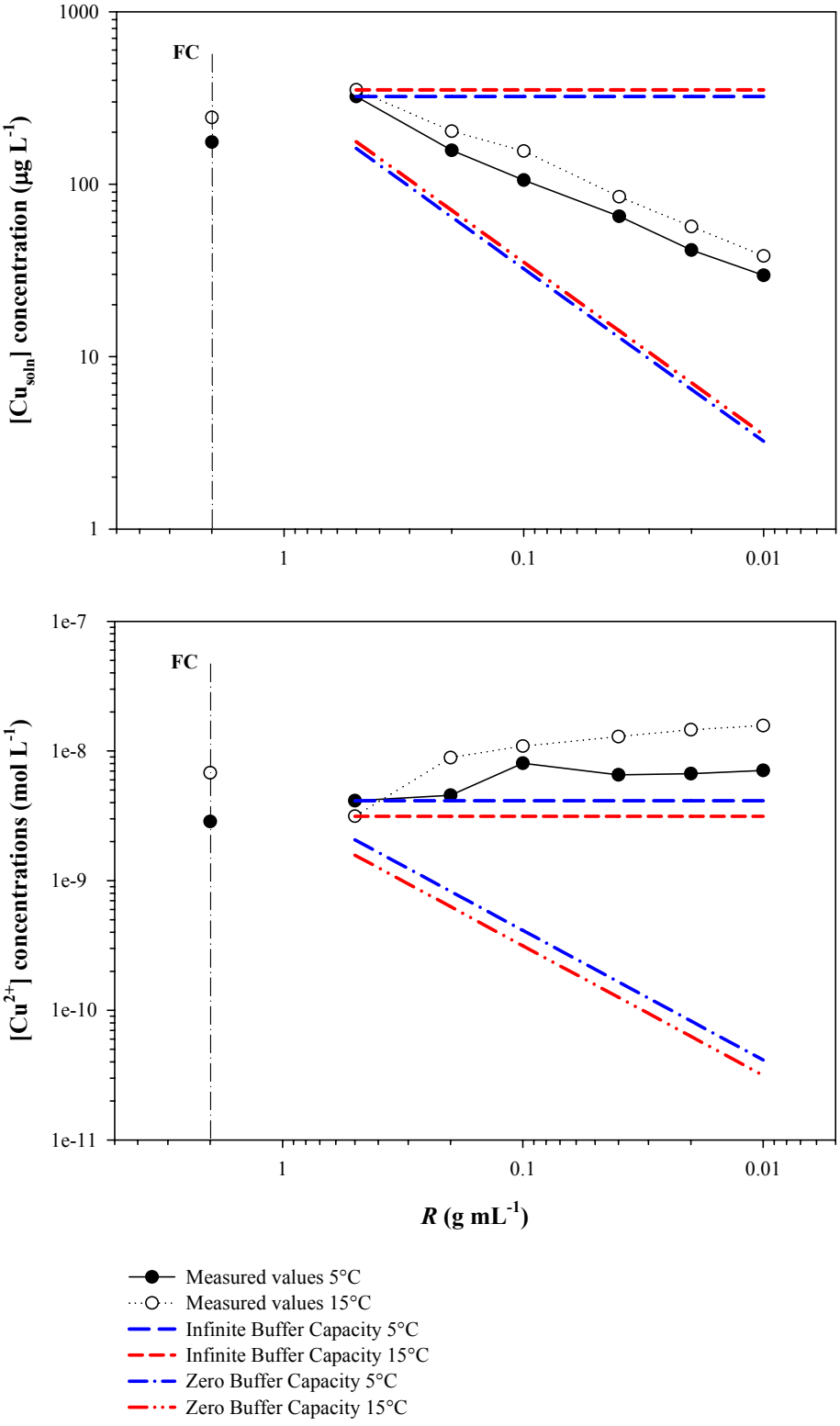


Figure 5.11. Total Cu and Cu^{2+} concentrations with varying soil:solution ratios compared to hypothetical 'infinite' or 'zero' buffer power.

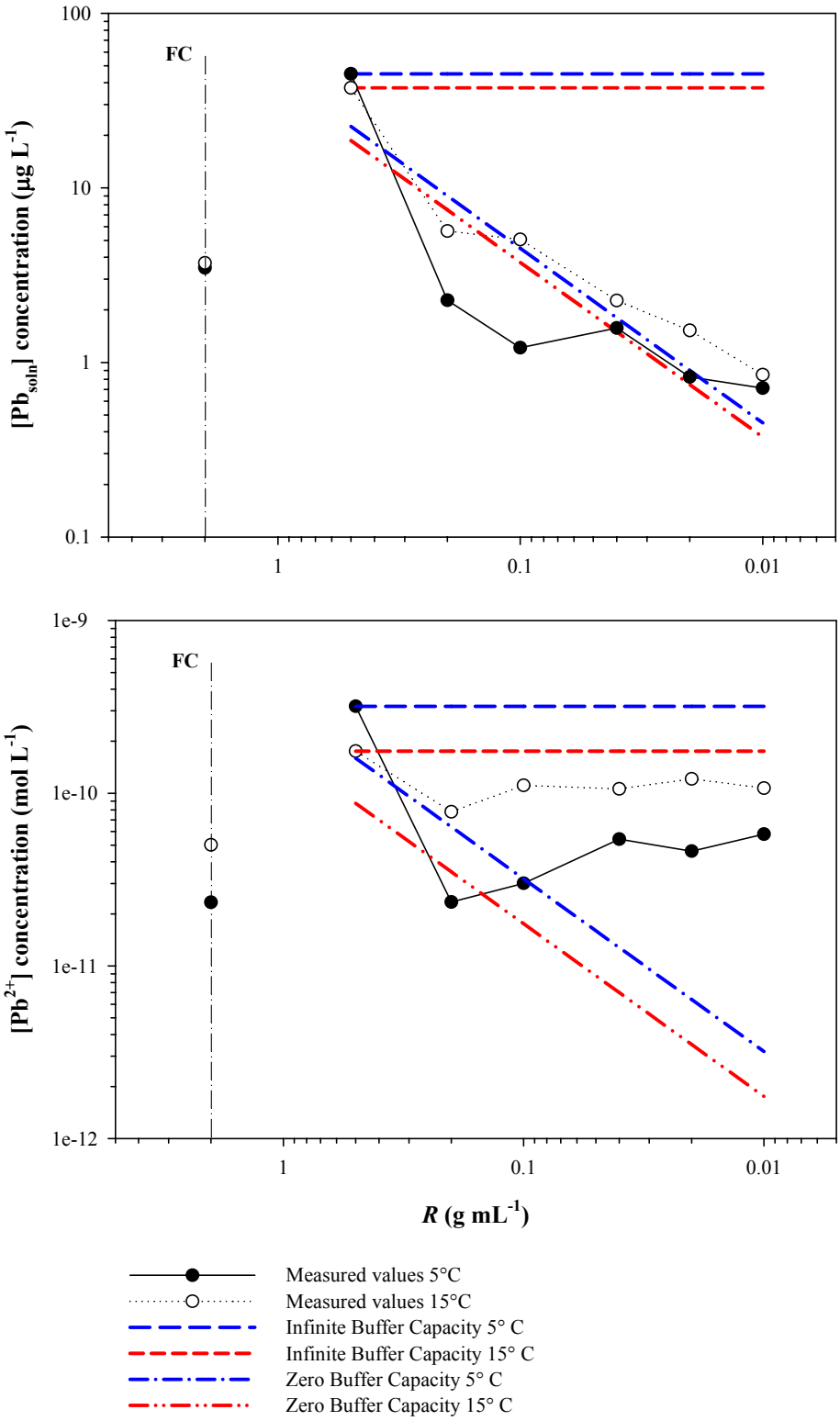


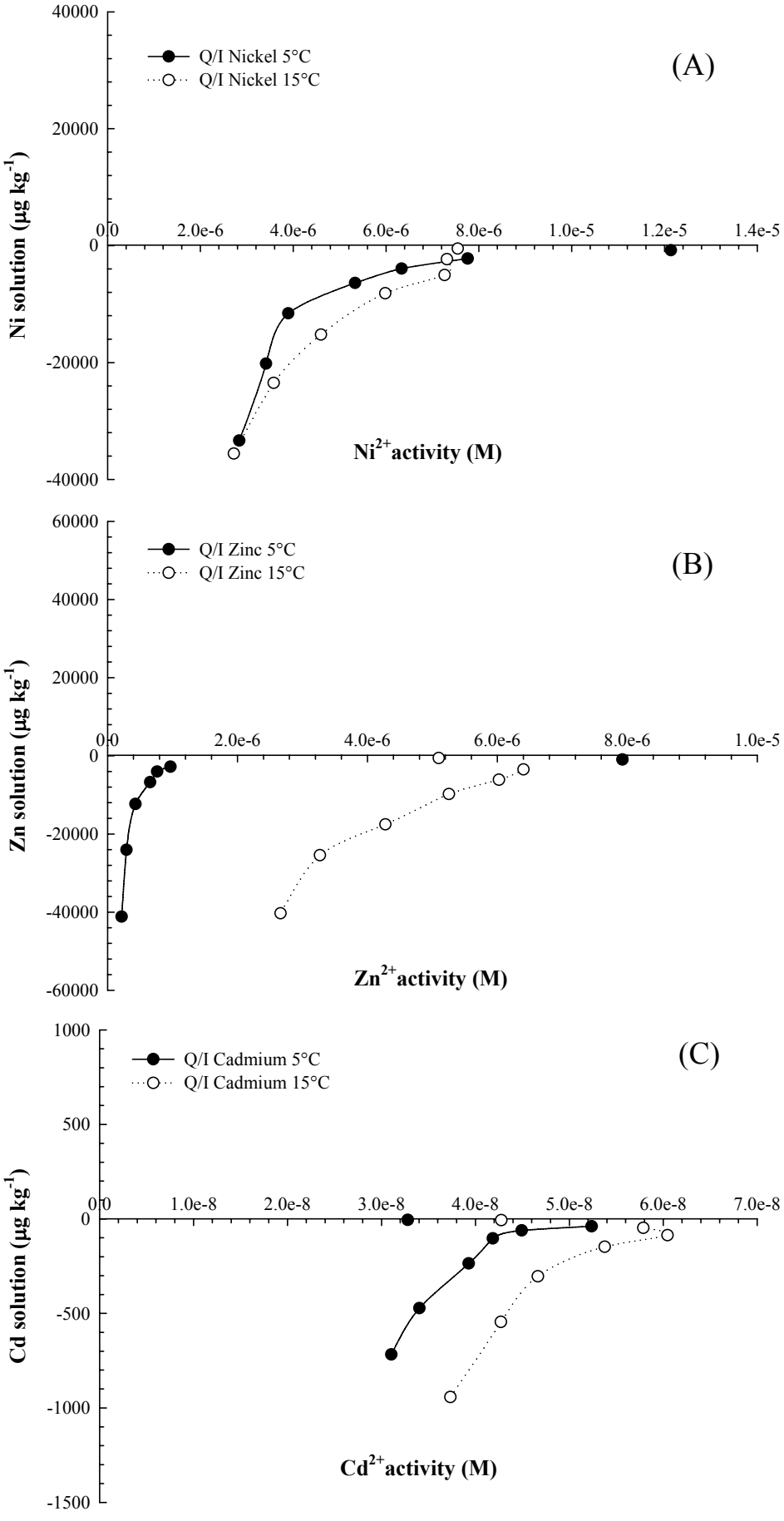
Figure 5.12. Total Pb and Pb^{2+} concentrations with varying soil:solution ratios compared to hypothetical 'infinite' or 'zero' buffer power.

5.4.1. Q/I relations

Fig. 5.13a-d presents the Q/I relations for Ni^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+} and Cu^{2+}. The plots are shown with the X-axis range reflecting the range of data measured. The soil buffer capacity determines the variability in the Intensity seen in response to solid phase depletion and is formally taken as the slope of the curve at $\Delta Q = 0$ (Beckett and Nafady, 1967). The curvature of the 'isotherm' indicates heterogeneity of adsorption strength and/or desorption hysteresis, where the steeper the slope, the more strongly buffered is the solution. The buffer capacity in field conditions should correspond to the slope where the line tangent to the curve joins the X-axis, whereas the intercept with the Y-axis indicates the labile metal content of the soil. By observing fig 5.13a-d it appears evident that the labile pools are accessed only in a very limited way with increasing dilution, as the intercepts for the isotherms are way down the Y-axis, which in turn implies that only a very limited portion of the metals is desorbed. Although soil slurries were shaken for 72 hours, perhaps this duration was not enough to allow for complete desorption to take place for lower values of ***R***. In natural soils, metals can be adsorbed onto particles as well as precipitated. The equilibration time is important to consider the kinetics that intervene in the mechanisms of solubilization of the metals, where kinetic dissolution are usually slower than kinetic desorption (Bordas and Bourg, 2000). The kinetic of desorption is obviously time-dependent, as shown by Millward and Liu (2003), whose study pointed out how dissolved Cd, Cu, and Ni increased within few minutes, followed by a plateau after several hours of incubation; desorption of Zn was characterised by a maximum followed by readsorption onto the suspended sediment. In addition, the equilibration temperature could play an importante kinetic effect, as testified by the case of Zn, which presented significantly different Q/I relationships between the two temperatures investigated. This might reflect either a difference in desorption kinetics or could be due to the greater $[Zn_{soln}]$ measured at 15°C. In fact, sorbed metals

are usually treated as "kinetically homogeneous", with no attempt to discriminate between chemically reactive (labile) metal and metal that is kinetically unreactive or physically occluded (nonlabile) (Tye *et al*., 2003). In general, the presence of humic substances is expected to play an important role in buffering of free metal ion concentration in soil, where the strongest (and least labile) sites will be those responsible for metal binding (Town and Filella, 2002) and desorption processes seem to be affected by hysteresis (Nye and Tinker, 1977).

The linearity or non-linearity of the Q/I plots is an indication of the homogeneity or heterogeneity of the sites affected by desorption, where processes and pools of metals involved could be different for varying ***R***. Ni^{2+}, Zn^{2+}, and Cd^{2+} present curvilinear isotherms, whereas Cu^{2+}, and Pb^{2+} isotherms show an unusual behaviour where free metal ion activity appears to increase with depletion. As observed in the previous section, the error in estimating (M^{2+}) is clearly going to be greater where the majority of M_{soln} is present as organic complexes (Cu and Pb) because DOC changes so significantly with ***R***. Furthermore, the magnitude of vatiation in (M^{2+}) across the range of ***R*** values is quite small (less than an order of magnitude). Generally, the steeper section of the isotherm can be attributed to desorption of adsorbed metals with relatively stronger bonding energies (Welp and Brummer, 1998). A flatter slope is associated with less specific sorption (Tiller *et al*., 1979), hence with pools of easily-exchangeable metals. Arnold (1970) points out that if the isotherm is curvilinear, the cation is being desorbed from high- and low-affinity sites. Alternatively, in presence of linear Q/I curves, the soil may contain a large amount of exchangeable M^{2+} such that it would mask the more specifically bound M^{2+} (Diatta *et al*., 2000). Such behaviour could be expected if the buffering properties of the soil were low.


(A)
Q/I Nickel 5°C
Q/I Nickel 15°C
Ni solution (µg kg-1)
Ni2+activity (M)
40000
20000
0
-20000
-40000
0.0
2.0e-6
4.0e-6
6.0e-6
8.0e-6
1.0e-5
1.2e-5
1.4e-5
(B)
Q/I Zinc 5°C
Q/I Zinc 15°C
Zn solution (µg kg-1)
Zn2+activity (M)
60000
40000
20000
0
-20000
-40000
-60000
0.0
2.0e-6
4.0e-6
6.0e-6
8.0e-6
1.0e-5
(C)
Q/I Cadmium 5°C
Q/I Cadmium 15°C
Cd solution (µg kg-1)
Cd2+activity (M)
1000
500
0
-500
-1000
-1500
0.0
1.0e-8
2.0e-8
3.0e-8
4.0e-8
5.0e-8
6.0e-8
7.0e-8

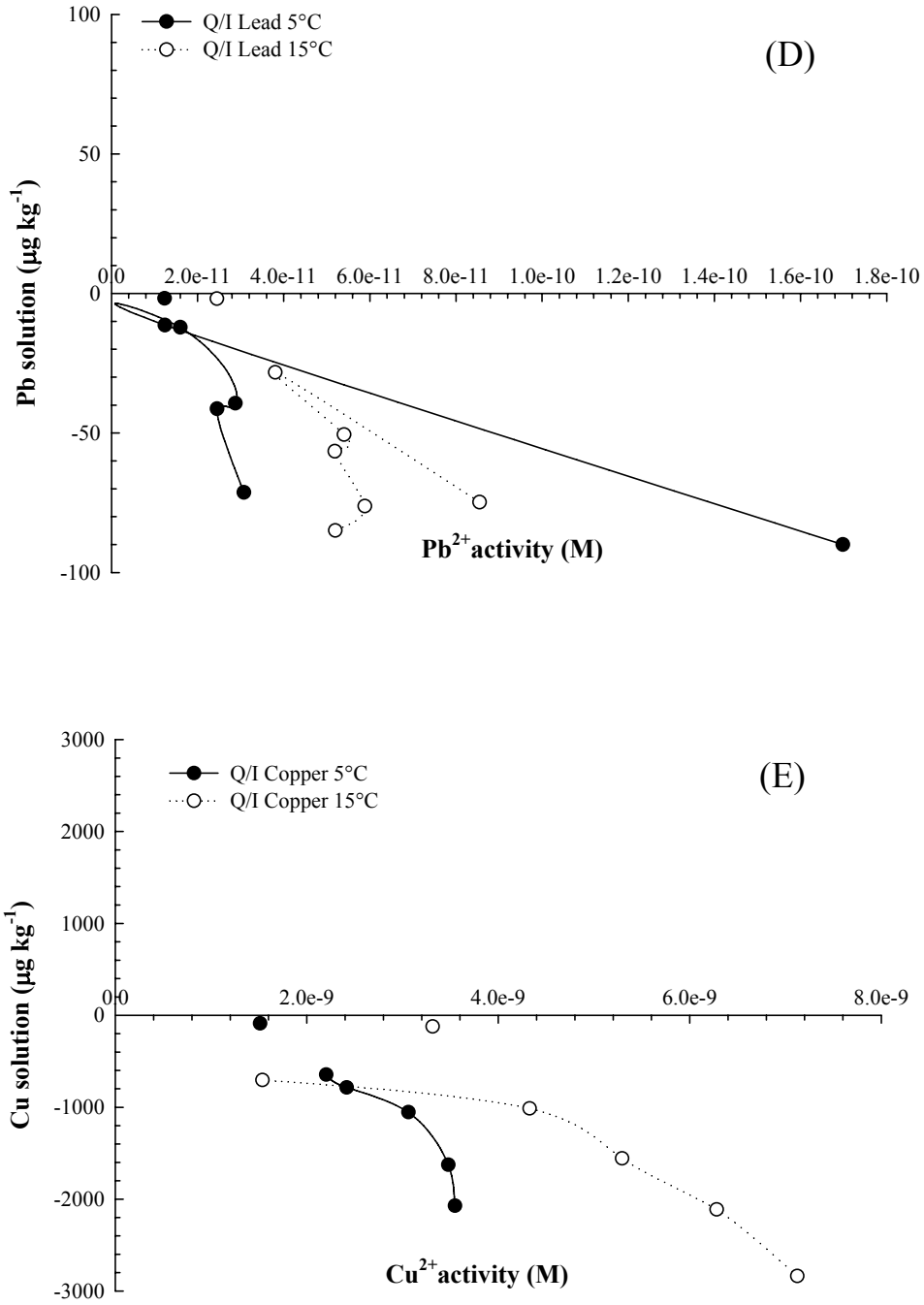


Figure 5.13. Quantity/Intensity plots for the metals studied; metals activities are as calculated by WHAM-VI (M); concentrations in solution represent the desorbed fraction and are calculated from total solution concentrations and divided by soil:solution ratios (µg kg^{-1}).

5.5. Conclusions

The effect of ***R*** on metal concentrations in soil pore water is of interest because it can characterize soil pore water at different water content, and also to explain the effect of different values of ***R*** in procedures for extracting equilibrium soil pore water. Water extracts are often used to measure pore water chemistry and thus extrapolating its equivalent composition at FC. However, this simple experiment showed that this could be an ambiguous exercise if not corroborated by sound speciation models. Surprisingly, despite the large initial metal and OM concentrations, the soil studied was barely able to buffer the concentrations of metal in pore water at increasing dilutions, with a very pronounced effect on DOC. Desorption of DOC is probably too slow to give a reliable or consistent value independent of ***R.*** On the other hand, there is good evidence that solubility/adsorption equilibria of free divalent metals are maintained reasonably well (relatively constant $[M^{2+}]$ and very limited depletion of labile pool). The significance of this is that it is possible to attain a fairly reliable estimate of bioavailable metal (M^{2+}) even in strongly dilute suspension but poor estimates of M_{soln} (e.g. for leaching studies) since they are hopelessly dependent on operational aspects of the suspension/extraction scheme.

The effect of other experimental variables can be largely eliminated, considering that ionic strength and composition of major cations and anions were not a variable in this experiment but only the values of ***R*** were modified. More studies are needed to clarify the effect ***R*** on metal and DOC solubilities and to investigate the reason for such an apparently poor buffer capacity with respect to the latter, perhaps by increasing the equilibration time to several days or weeks to assess if hystheresis would still be so pronounced. Otherwise, suspensions with high solids concentrations should be used for batch experiments extractions to approach more closely natural conditions, unless only estimates of free metal ion activity (M^{2+}) are needed.

6. Using labelled water to assess sources of sampled soil water

6.1. Introduction

It is commonplace to find different solute concentrations in soil water samples from different sampling procedures, such as suction and gravity samplers, centrifugation and column displacement (see Chapter 3). These differences have often been attributed to the fact that the sampling procedures collect water from different pore sizes and thus represent different fractions of the total soil water (Landon *et al*., 1999). It is speculated that the different fractions of soil water have different mobility, and hence, different compositions since the water is moving at different rates along different pathways (Jardine *et al*., 1990; Harvey, 1993). The immobile (or inaccessible) water domain exists in micropores and thin films around soil aggregates and is so defined because such soil water can be considered less mobile, in comparison with water in the 'mobile' (or accessible) zone. Many studies have documented the existence of water fractions of different mobility in the unsaturated zone in laboratory columns, modelling, and field studies (Coates and Smith, 1964; Van Genuchten and Wierenga, 1976; Gaudet *et al*., 1977). In an unsaturated soil medium with a given degree of heterogeneity, preferential flow tends to be dominant at low water contents while piston flow dominates at higher water content (Padilla *et al*., 1999). Therefore, if the soil system is at FC, with capillary forces governing water movement (with respect to gravitational forces), preferential flow mechanisms are likely to prevail. In the simplest case of preferential flow (as opposed to piston flow), water is considered to have a bimodal distribution of velocities, corresponding to more or less mobile (accessible) phases (Tang and Feng, 2001). Furthermore, the composition of the soil pore water depends on the efficiency of the solute mixing process, which further depends upon water interaction mechanisms in different pore classes. Less

accessible water is viewed as residing in dead-end pores, thin liquid films around solid particles, and immobile intra-aggregate water (Kutilek and Nielsen, 1994) (Fig 6.1).

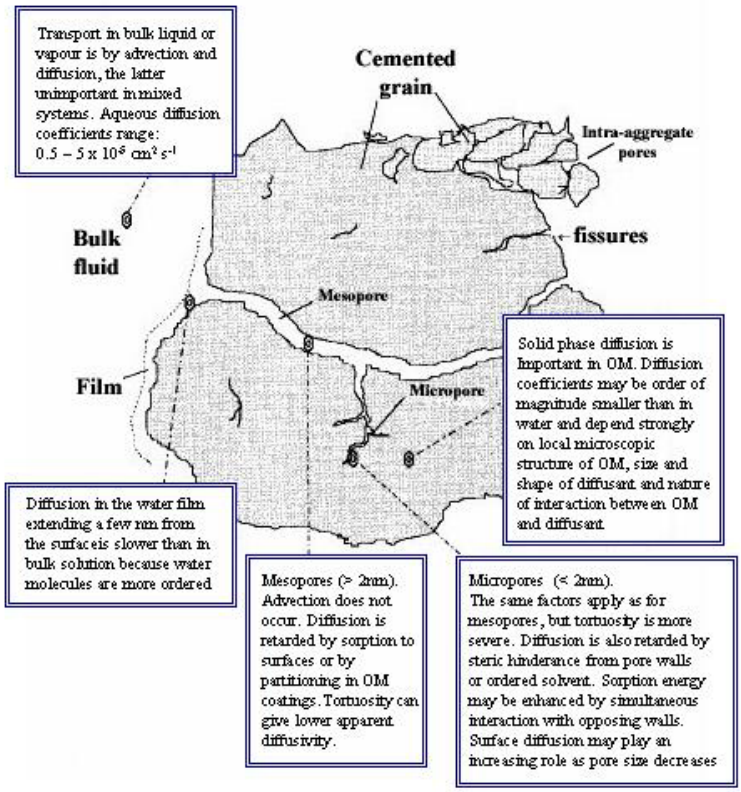


Figure 6.1. Schematic of a soil particle aggregate showing the different diffusion processes. (from Pignatello and Hing, 1996, modified).

Less accessible water can be transported only by exchanging and mixing with more mobile water during percolation (diffusion); the rate of this exchange/mixing may be characterized by a first order exchange rate coefficient (Coates and Smith, 1962). This spreading phenomenon is also known as hydrodynamic dispersion, occurring as a consequence of inhomogeneous flow in a porous medium (i.e., difference in pore size, tortuosity, mechanical mixing) and molecular diffusion (i.e., flow velocity in individual pores) (Freeze and Cherry, 1979). Furthermore, water is associated with soil solids in different physical states such as water vapour, adsorbed water, interlayer water, as well as water in the form of hydroxyl groups that

are an integral part of the mineral or organic structure. The first shell of water around a strongly solvated (hydrated) ion or surface group is known as the primary hydration shell. This is where the water molecules are most restricted in their motion. The bound water molecules are thought to exchange with bulk water, but only relatively slowly (Horseman *et al*., 1996).

However, the effect of the ion solvation (hydration) propagates out well beyond the first shell, each subsequent shell of water molecules exhibiting a greater capacity to change orientation and to exchange with the bulk water. Depending on their size and charge, ions can influence the scale of these exchanges. Ions such as Li and F are 'structure-makers', as a result of their high polarizing power, whereas larger ions can have the opposite effect ('structure-breakers'). The presence of nonpolar solutes, such as small hydrocarbon molecules, gives rise to an increase in the degree of structuring, i.e. mixing/exchanging. Quasi-elastic neutron scattering (QENS) studies provided powerful insight to mobility of adsorbed water molecules in thin films (e.g. Tuck *et al*., 1985), showing that adsorbed water has a mobile component, undergoing rapid but spatially-restricted diffusion, and a 'relatively immobile' component (slower diffusion) corresponding with water molecules in the hydration shells of surface cations. Therefore, if waters of different isotopic compositions is added to the same soil system, an isotopic effect may be expected as water is transferred from one of these physical states to another (Stewart, 1972), which may also discriminate between more or less 'accessible' water referring to different pore sizes.

In this chapter, two of the pore water sampling procedures used in this study (Rhizon samplers and centrifugation) are assessed in terms of their ability to differentiate between 'accessible' and 'inaccessible' water and to what extent these two types of water exist and interact with each other in the soil studied. Samples of the Stoke Bardolph soil were dried to a known matric potential (300 kPa, corresponding to 33.2% gravimetric water content)

and then rewetted to FC using water isotopically enriched in ^{18}O. At this stage the soil contained both un-labelled water (remaining after partial drying) and the labelled water added during rewetting. Pore water samples were collected, using Rhizon samplers and centrifugation, and the total residual water extraction was then undertaken by *in-vacuo* freezing distillation. All samples were assayed for their $^{18}O/^{16}O$ ratios to provide information on the relative distribution and mixing of added labelled water.

6.2. Isotopic exchange in soil water

6.2.1. Oxygen in water and soils

The stable oxygen isotope composition of the water, its $^{18}O/^{16}O$ ratio, is used as a conservative tracer of water in many circumstances because it is uniquely intrinsic to the water molecule and thus can help elucidate the origin, phase transition, and transport of H_2O (Criss, 1999). Since they are amenable to theoretical modelling using the laws of physical chemistry, oxygen isotope ratios have often been used to identify the sources and pathways of water in the unsaturated zone, to describe movement and transport of chemical weathering products, contaminants, and nutrient cycles that are strongly tied to hydrological conditions (Darling and Bath, 1988; Tang and Feng, 2001; Gazis and Feng, 2004).

6.2.2. Isotopic ratio

Because variations in isotopic abundances can be relatively small, stable isotope ratios are usually reported as a ratio relative to a standard as δ values in units of part per thousand (per mill, written ‰). The general expression for stable isotope notation is (Coplen *et al.*, 1999):

$$\delta_x(\text{in ‰}) = \delta_{x-std} = \left[\frac{R_x}{R_{std}} - 1\right] \times 1000 \qquad (6.1)$$

where R_x and R_{std} are the heavy/light isotope ratios of the sample and standard, respectively. Thus, for oxygen isotopes:

$$\delta^{18}O(\text{in ‰}) = \left[\frac{{}^{18}O/{}^{16}O_{sample}}{{}^{18}O/{}^{16}O_{VSMOW}} - 1 \right] \times 1000 \qquad (6.2)$$

VSMOW (Vienna Standard Mean Ocean Water) being the international standard ($^{18}O/^{16}O$ of VSMOV = 2005.2 ppm). Hence, an oxygen sample whose $\delta^{18}O$ value is +50.0 ‰ is enriched in ^{18}O by 5 % or 50.0 ‰ relative to the standard; the sample is isotopically 'heavy' relative to the standard. A negative δ value indicates the sample is depleted in the heavy isotope relative to the standard; the sample is isotopically 'light' relative to the standard.

6.2.3. Processes leading to variations in soil water concentration

The movement of ^{18}O in soils may be discussed in terms of the same physical models used to describe water movement in soils. In essence, in the liquid phase, water is considered to move in response to potential gradients according to Darcy's law, and the heavier molecular weight isotopic species of water are modelled as a simple solute undergoing **convection**, **dispersion** and **molecular diffusion**. In the vapor phase, all isotopic species of water diffuse as ideal gases in response to concentration gradients, according to Fick's law.

Isotope fractionation may result from small differences in diffusivities (particularly in vapor phases), and also from differences in the saturated vapor pressure between different isotopic species. This model is sufficient to develop a general theory of isotope movement in unsaturated soils and to explain a wide range of experimental data.

Knowledge of the oxygen isotope fractionation between liquid water and water vapour is essential for the interpretation of the isotope composition of

different water types (Hoefs, 1998). Experimentally determined fractionation factors (from 0 to 350°C) have been summarized by Horita and Wesolowski (1994).

6.2.4. Soil water extraction for isotope analysis

Fractionation can also be caused by the extraction technique. Vacuum distillation, azeotropic distillation, microdistillation with Zn, and immiscible displacement using centrifugation are commonly used for this purpose. Walker and Woods (1994) reported a number of comparisons, suggesting that the extraction technique may have a large bearing on the measured isotope ratio. An observed range of up to 30‰ in δD (the ratio for hydrogen isotopes) and 3.5 ‰ in $\delta^{18}O$ was shown to be correlated with the temperature of extraction of the technique used, and was ultimately associated with incomplete extraction. The consensus appears to be that all extraction techniques potentially result in some fractionation**,** and it is necessary to attempt to extract as much water as possible from a soil sample in order to obtain useful results. Fractionation effects appear to be more pronounced for the more strongly bound water, which is produced toward the end of the extraction period. The effect is greater for soils with a large fraction of small pores (i.e. high specific surface area), such as clays and clayey soils. Uncertain results are also obtained for soils, which contain a high proportion of hydrated salts, such as gypsum, due to inconsistent partial salt dehydration on extraction. It is therefore important to extract the residual water as completely as possible to minimize this effect (see Materials and methods).

6.3. Materials and methods

6.3.1. Sample preparation

Soil samples from the same batch as described in previous chapters were used (i.e. Stoke Bardolph soil, initially under field-moist conditions).

Three separate soil sub-samples were separated from this initial batch to measure the initial 'undisturbed' isotopic composition ($\boldsymbol{R_i}$), and their water weight and moisture content recorded respectively as $\boldsymbol{W_i}$ and $\boldsymbol{\theta_{FC}}$.

Three more sub-samples of 500 g each were then taken from the initial batch at FC and dried down to 33.2% water content (moisture content - MC) (Dry Weight Basis) at 10° C and 98% humidity in an environment chamber (Model 518, Electro-Tech Systems, Inc.), capable of controlling the relative humidity over the range 5 – 98% and the temperature over the range 0 - 50° C. This water content was chosen on the basis of the measured moisture release curve for the soil studied (see sections 2.5.2.3. and 2.6.1.) because it corresponds to 300 kPa matric potential, which represents the boundary between storage and residual pores (see Fig. 2.12). Three more sub-samples of 35 g each were removed from the dried batch and prepared for water extractions to derive their gravimetric water content (%) and weight (g) ($\boldsymbol{\theta_{dry}}$ and $\boldsymbol{W_{dry}}$) and isotopic composition ($\boldsymbol{R_{dry}}$, ‰ δ ^{18}O VSMOW).

The partially dried batch of soil was then rewetted to FC using labelled water with a known ^{18}O composition (+40.6 δ ^{18}O VSMOW ; $\boldsymbol{R_{label}}$). The amount of water to add was calculated on the basis of the moisture release curve, and this fraction was recorded as $\boldsymbol{\theta_{label}}$. Labelled water was added with a syringe whilst mixing the soil slowly (using a food mixer). Three sub-samples were separated, measured for gravimetric water content and weight ($\boldsymbol{\theta_{fin}}$ and $\boldsymbol{W_{dry}}$) and kept to derive isotopic composition ($\boldsymbol{R_{fin}}$, ‰ δ ^{18}O VSMOW) from the equilibrated wetted soil as soon as the rewetting operation terminated. The batch of soil rewetted to FC was then immediately prepared for pore water sampling using Rhizon samplers and centrifugal extraction as previously described (sections 3.4.2.4. and 3.4.3.3.).

Soil pore water was removed by Rhizon samplers and centrifugation at 2000, 4000, 6000 and 7000 rpm (i.e. 70, 281, 632 and 860 kPa) using 100 g of soil and standard procedure (T = 15^{o} C, t = 1 h) and their weight recorded as $\boldsymbol{W_{rhi}}$ and $\boldsymbol{W_{cen}}$. The fraction of water removed was recorded and called $\boldsymbol{\theta_{mobile}}$.

Three soil sub-samples were also taken at the end of the extractions and the weight and fraction of residual water derived ($W_{resid\text{-}r}$, $W_{resid\text{-}c}$, $\theta_{resid\text{-}r}$ and $\theta_{resid\text{-}c}$) for isotopic analyses ($R_{resid\text{-}r}$ and $R_{resid\text{-}c}$), where the suffix *r* and *c* denote rhizon samplers and centrifugation respectively. The fraction of water remaining (θ_{resid}) was measured. The overall $^{18}O/^{16}O$ isotope ratio for the system (R_{system}) was computed from the sum of the isotopic ratio of its components (R_j), each multiplied by the appropriate weighting factor (X_j), which was derived following equations (6.3) and (6.4) (Criss, 1999):

$$R_{system} = \sum_{j=1}^{n} X_j R_j \tag{6.3}$$

and

$$\sum_{j=1}^{n} X_j = 1 \tag{6.4}$$

where X_j refers to mole fractions, calculated in terms of ^{18}O.

Therefore, for the mass balance we should expect:

$$(\theta_{FC} \times W_{fin}) = (\theta_{resid} \times W_{resid\text{-}r}) + (\theta_{mobile} \times W_{rhi})$$

and

$$(\theta_{FC} \times W_{fin}) = (\theta_{resid} \times W_{resid\text{-}c}) + (\theta_{mobile} \times W_{cen})$$

In the case of isotopes in a simple mixture of n end-members, the appropriate mole fraction X_k of end-member *k* may be expressed in terms of the mass fractions M_j of all the various end-members, and the concentrations C_j of the element of interest in each end-member as follows:

$$X_k = \frac{C_k M_k}{\sum_{j=1}^{n} C_j M_j} \tag{6.5}$$

Therefore, in the case of complete mixing between the pre-existing water and the freshly added labelled water, one can expect the final composition to be calculated from equation (6.6):

$$\boldsymbol{R}_{\infty} = (\boldsymbol{\theta}_{dry} \times \boldsymbol{R}_{dry}) + (\boldsymbol{\theta}_{label} \times \boldsymbol{R}_{label}) \tag{6.6}$$

where

$\boldsymbol{R}_{\infty}$ = final isotopic composition assuming complete mixing between the two endmember ($\delta^{18}O$, in ‰);

$\boldsymbol{\theta}_{dry}$ = gravimetric fraction of water at initial composition after drying soil samples at $\boldsymbol{\theta}$ = 0.332 (residual water);

$\boldsymbol{\theta}_{label}$ = gravimetric fraction of labelled water freshly added;

$\boldsymbol{R}_{dry}$ = isotopic composition of residual water ($\delta^{18}O$, in ‰);

$\boldsymbol{R}_{label}$ = isotopic composition of labelled water ($\delta^{18}O$, in ‰).

Using this approach it is possible to calculate mixing rates for the movement of labelled water into the native soil water, using the following formula:

$$F_j \ mixed \ \ (in\%) = \frac{\theta_{label}\left(R_{label} - R_j\right)}{\theta_{dry}\left(R_j - R_{dry}\right)} \tag{6.7}$$

where $\boldsymbol{F}_j$ is the fraction of native water mixed with the labelled added water, and $\boldsymbol{R}_j$ represents the measured isotopic composition.

Care was taken at all times to avoid unnecessary sample exposure, particularly in a humid atmosphere where losses of label may be significant even though little net evaporation takes place. All soil samples were sealed rapidly in airtight containers in order to avoid sample modification due to evaporation and isotopic fractionation. Samples were also weighed as soon as possible after initial storage. Samples stored for longer length of time

before extracting water samples were re-weighed before analysis and those with significant weight loss were discarded. A small amount of evaporation can significantly modify the isotopic composition of samples: typically, a 1% weight loss due to evaporation might result in a 1‰ and 0.4 ‰ increase in δD and $\delta^{18}O$, respectively, for the remaining sample (Barnes and Turner, 1998).

6.3.2. Residual water extraction

Residual water extractions for isotopic analyses were carried out using a static, *in-vacuo*, freezing method, using facilities designed by Dr. Tim Heaton at the British Geological Survey.

The samples were initially loaded into the test-tubes (Fig. 6.1, on the right), and capped with a rubber bung to stop moisture loss. The tube had an i.d. of 15 mm, and a volume of about 20 ml. The tubes were loaded inside the right arm of the glassware apparatus, and both arms clipped to the vacuum seals on the cross-piece.

With the top vacuum valve closed, the right arm is frozen in liquid N_2, the apparatus attached to a vacuum pump, and the top valve then opened to remove all air. The right arm (frozen soil) is then placed in a tube furnace at about 90˚C, with the left arm in liquid N_2, for about 8 hours; the top vacuum valve is then opened to extract the (evaporating) frozen water into the left arm.

Residual water samples were then collected and placed in tightly-capped 4 mL glass bottles without any further treatment and kept in a 4°C fridge prior to analysis.

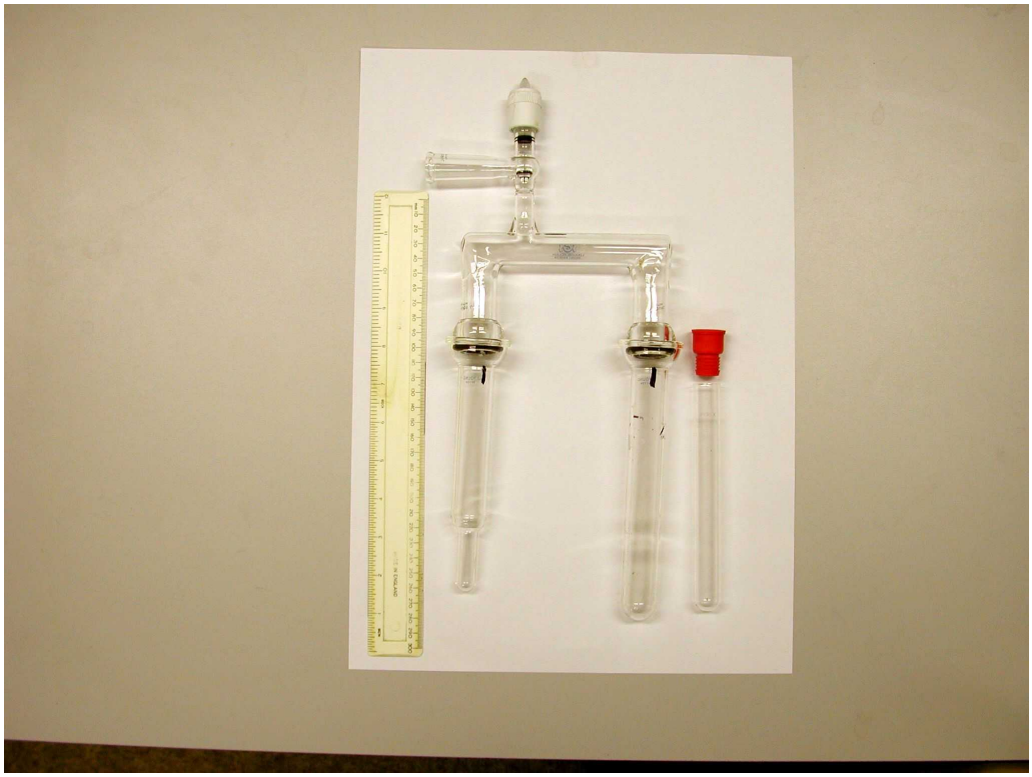


Figure 6.2. Test tubes and glassware apparatus for *in-vacuo* freezing extractions.

6.3.3. Analysis, isotopic ratios and data reporting

Analysis for ^{18}O was undertaken using the equilibration method for oxygen (Epstein and Mayeda, 1953) with a VG Isoprep 18 and Sira 10 mass spectrometer at the NERC Isotope Geoscience Laboratory, Keyworth.
Oxygen isotope values for water samples were calculated using equation 6.2 and reported relative to VSMOW (‰). Analytical precision was typically ±0.05‰ for $\delta^{18}O$. The proportion of native water which has effectively mixed with the added labelled water at the time of sampling was calculated from equation (6.7).

6.4. Results and discussion

Results seem to suggest a rapid and almost complete mixing of the two types of water (residual and labelled) involved in the experiment. Figure 6.3

shows the compositions of the pore waters extracted by Rhizon samplers and centrifugation compared to the initial and freshly added water compositions. The final 'complete mixing' composition ($\boldsymbol{R}_{\infty}$), calculated using equation (6.6), was +11.7‰ SMOW, and is represented by the horizontal red line. This result was in full agreement with the measurements undertaken on sub-samples separated prior to Rhizon and centrifuge extraction. Total pore water was extracted from these sub-samples by *in-vacuo* freezing method and analysed for isotopic ratio, resulting in a total composition of +11.8‰ VSMOW.

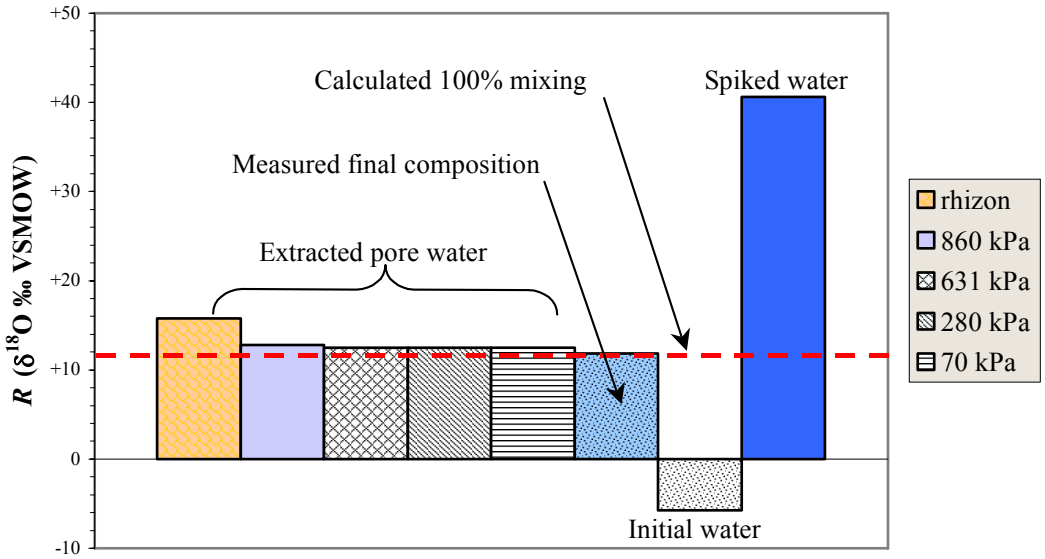


Figure 6.3. Isotopic composition (***R***) of pore water extracted by Rhizon samplers and centrifugation at 15° C; initial and spiked water compositions are given; centrifugation speed used: 2000, 4000, 6000 and 7000 rpm; the red line is showing final 100% mixing between native and added labelled water, calculated using equation (6.6).

Pore water samples extracted by rhizon samplers appear to be slightly enriched in ^{18}O, suggesting some 'fractionation' during the extraction or ability by the method to target labelled H_2O. The values observed for the 4 centrifugal steps are slightly different, with greater proportions of ^{18}O occurring with increasing centrifugal speed employed. However, these differences are very small (see also Table 6.1), underlying that this method is

capable of extracting very homogeneous samples. In fact, the process of centrifugation itself is likely to produce or enhance water mixing throughout the soil sample, explaining the homogeneity of the water extracted. This is confirmed by the δ values of the residual water remaining after the centrifugation, which are very similar to the final mixed composition ($\boldsymbol{R}_\infty$) (+11.7‰). By contrast, the δ values for the pore water extracted by Rhizon samplers appear significantly more enriched in ^{18}O compared to those extracted by centrifugation. This can be better observed in Fig. 6.4, where the fractions of native water and added labelled water mixed together were calculated on the basis of equation (6.7).

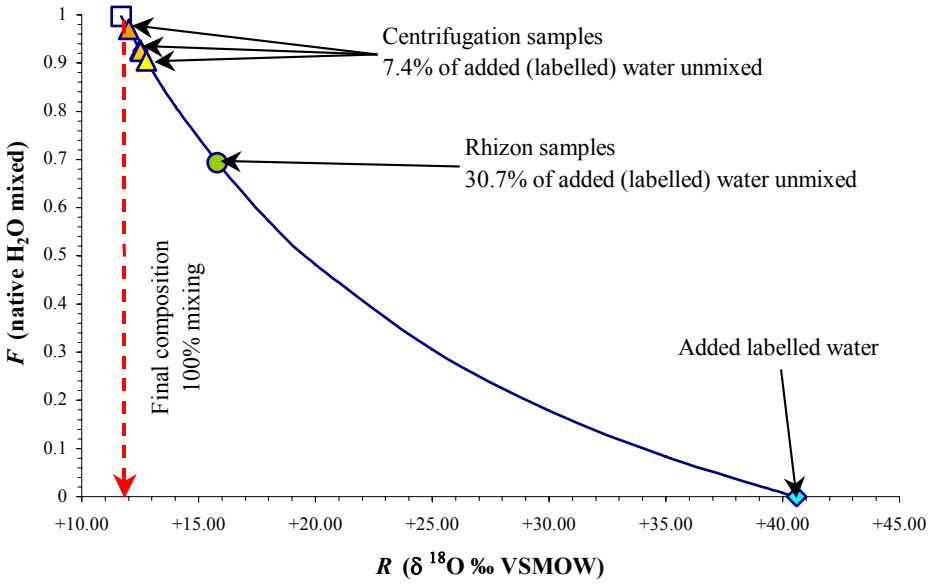


Figure 6.4. Calculated curve showing increasing mixing between added labelled water (0% mixing) and native water (initial composition $\boldsymbol{R}_{dry}$ = -5.77 ‰ VSMOW); final composition $\boldsymbol{R}_\infty$ = +11.7 ‰ VSMOW. Isotopic composition and corresponding fractions of unmixed native water are given on the Y-axis (***F***); the red line is showing final 100% mixing between native and added labelled water.

Thus, there seems to be a significant difference between the two methods of pore water extractions. Centrifugation is likely to produce an apparent 'infusion' effect, where more accessible water is forced to mix with less accessible water residing within the aggregates and/or in dead-end pores.

This contrasts with the extra-aggregate sampling nature of the Rhizon samplers: pore water sampled in this way showed a composition corresponding to 70% mixing with native water compared with the almost 93% mixed water extracted by centrifugation (Fig. 6.4) over the period of the trial (ca. 8 hours).

Furthermore, replications of both the mass of water extracted and their respective $\delta^{18}O$ compositions and the efficiency of the *in-vacuo* extraction of the residual water, were very good: the analytical error was negligible (typically ±0.05‰, see Table 6.1) and there were no further weight losses when the soils were completely oven-dried after completing the *in-vacuo* extraction. This suggests that any 'fractionation' artefacts were not due to incomplete extraction of water by the *in-vacuo* extraction mechanism but does not rule out evaporation during rhizon sampling or centrifugation. In fact, a fractionation caused by the extraction would be reflected in an equivalent depletion of ^{18}O in the residual water.

6.4.1. Isotopic fractionation

The fractionation factor (α) can be calculated to account for possible discrepancies. This is defined as:

$$\alpha_{A-B} = \frac{1000 + \delta_A}{1000 + \delta_B} \tag{6.8}$$

where A and B are the two phases or fractions involved. This difference in isotopic content may be also denoted by Δ, and is approximated by

$$\Delta_{A-B} = \delta_A - \delta_B \approx 1000 \ln \alpha_{A-B} \tag{6.9}$$

because $\ln(1+x) \approx x$ for small values of x.

Table 6.1 shows the differences between the isotopic content of the extracted pore water and that of the added 'doped' solution of fractionation

factors. The isotopic fractionation is clearly minimal in the all the extracted fractions, including those extracted by Rhizon samplers. In theory, conditions for this extraction method (the soil container during the extraction is left open to atmosphere at controlled temperature, 10° C) may have favoured evaporation, resulting in greater fractionation.

Table 6.1. Fractionation factors and difference in compositions between samples and residual waters; mass of water extracted (%) are reported.

Sample	Mass %	$\delta^{18}O$ ‰ VSMOW	α_{A-B}	Δ_{A-B}	Diff ‰ VSMOW
Initial	62.4	-5.77 ± 0.11			
Doped	37.6	+40.61			
Final	100	+11.84 ± 0.059			
R	13.5	+15.79 ± 0.011	1.0039	3.8968	+3.95
C1	13.1	+12.49 ± 0.037	1.0006	0.6447	+0.65
C2	12.6	+12.51 ± 0.020	1.0007	0.6604	+0.67
C3	13.3	+12.52 ± 0.024	1.0007	0.6696	+0.68
C4	13.6	+12.76 ± 0.079	1.0010	0.9115	+0.92
Residual	47.4	+11.75 ± 0.055	0.9999	-0.0885	-0.09

Other studies (e.g. Araguás-Araguás, 1995) showed the importance of fractionation effects accompanying incomplete extraction of soil water. However, the calculated α values for the extracted water samples suggest that fractionation due to evaporation was not a significant process during the water extractions and that the differences in isotopic composition could be attributed to different mechanisms of sampling.

6.4.2. Solute and water diffusion

Results suggest that diffusion of water occurred somewhat rapidly and that complete mixing of the two water phases (initial and doped) may be reached within the time of sample preparation. The presence of 'inaccessible' water, and therefore the amount of water which remains 'unmixed', is questionable, which therefore renders difficult its quantification by the methods of pore water extraction employed. Reported diffusion coefficients

for water in soils lie between 0.5 x 10^{-5} and 5 x 10^{-5} cm^2 s^{-1} (Pignatello and Xiang, 1996, see also Fig. 6.1), whereas the self-diffusion coefficient of water (at 25° C) is 2.4 x 10^{-5} cm^2 s^{-1} (Domenico and Schwartz, 1990). However, the diffusion coefficient in a porous medium is usually smaller than in pure liquids primarily because collision with the solid of the medium hinders diffusion, being controlled (and reduced) by factors such as porosity and tortuosity (i.e. the average ratio of the microscopic path length L to the macroscopic path length x in the medium, Horseman *et al.*, 1996). On the other hand, Conca and Wright (1990 and 1992) proposed that the diffusion of free water, i.e. not including any structural water in the calculations, could be estimated by means of volumetric water content only, using the equation:

$$\log_{10} D = -8.22 + 1.42(\log_{10} \vartheta) + 0.32(\log_{10} \vartheta)^2 \qquad (6.10)$$

where D is the diffusion expressed in cm^2 s^{-1} and θ is the 'free' volumetric water content. The Stoke Bardolph soil presented 12.7% volumetric hygroscopic water (see Table 2.5; ρ_b = 0.67), which for simplicity could be assumed to be 'structural' water. Therefore, at FC the free volumetric water content would be 22.8%, giving a value of D of $10^{-5.7}$ cm^2 s^{-1} from equation (6.8). This seems more or less in agreement with theoretical diffusion coefficients presented above. Perhaps the presence of partially dehydrated OM favoured the molecular diffusion of water, easing the alignment of water dipoles along the electric field vector, or simply by increasing the total porosity of the system, therefore increasing diffusion.

6.5. Conclusions

Rhizon samplers and centrifugation, the latter applied at increasing pressures, presented proof of different mechanisms of soil pore water sampling from different sources within the soil system. Evidence showed that centrifugation was not able to differentiate between more and less

mobile water at FC conditions on the soil studied (Stoke Bardolph), rather enhancing the mixing between the two pools of water (native and labelled) by and apparent process of 'infusion'. The water sampled by centrifugation was almost completely mixed with the native water. By contrast, Rhizon samplers appeared to sample water preferentially from the more accessible pool (extra-aggregate), which proved to have a composition showing incomplete mixing with the native water. The results also suggest that mixing of the two pools was rather fast and that was almost completely attained prior to pore water extraction, probably enhanced by OM and the associated increased porosity due to its presence. It seems reasonable that the interaction between tracer ($H_2{}^{18}O$) and solid surfaces would depend upon moisture content and would be greater during flow of labelled water into initially dryer soil than during miscible displacement flow in saturated soil (Stewart, 1972). The literature did not present any study to corroborate this hypothesis, since most cases were conducted through column experiment and at near-saturation conditions. As a consequence, solute isolation from different pore classes as an explanation for differences in chemistry during multiple pore water extractions, could be difficult to sustain given these results. In fact, considering the differences in pore water chemistry noted in chapter 4 in the light of the present results, one may conclude that centrifugation samples should represent homogenised waters due to the extraction process itself, therefore showing little differences in solute concentration. The few centrifugation samples presenting different solute concentration were normally coinciding with the very first extractions step (lower speed, higher moisture content), and for selected elements (Al, B, Ba, Co, Cr, K, Na and to a lesser extent Pb, Sb, Sr and Zn). These differences could be explained by the particular chemical condition present at that stage of the extraction, with the OM playing then a greater influence on element mobility that during the rest of the centrifugal extraction, but not necessarily to different pore classes been witdrawn (more accessible water).

Questions could be raised regarding the experimental design and the choice of residual water content as well as the mechanism of addition of the labelled water. The latter could have enhanced the mixing of the two phases, although no other or more efficient system to add the water to the soil in a homogeneous way could be found. Furthermore, the use of the same soil sample for soil pore water extraction by centrifugation might have induced some mixing of waters for successive extracted fractions during this process. Since the extraction by centrifugation is not instantaneous but takes at least 1 hour (it could be decreased to 30 minutes), this time is also likely to play a role in the diffusion of the labelled water within the soil system. In addition, during the process of centrifugation itself, the rate of diffusion of the labelled water to the smaller pores is likely to increase dramatically, making the interpretation of the results difficult in terms of time of diffusion. This is confirmed by the homogeneity of the pore water collected, as shown by $^{18}O/^{16}O$ ratios.

7. Conclusions

The objectives of this thesis were to investigate methods for sampling soil pore water with particular focus on trace elements, to interpret differences between these methods and to establish whether there were any effects of pore size and heterogeneity on observed concentrations. In addition, a study was made to establish whether the pore water extracted was actually representative of the 'true' conditions in a soil system or whether artefacts were introduced at various stages during sample preparation and handling. This was achieved by comparing 4 methods, all of which have benefits/constraints, i.e. sampling various soil water components and providing different levels of information.

The project outcomes are assessed below in the context of the stated aims:

- Successfully developed and tested a novel extraction method
- Critically evaluated 3 existing methods
- Studied the results in relation to the concept of soil macro- and micropores
- Compared time/cost and outcomes of the methods
- Demonstrated that all can be useful, depending on what the aims and intended use of the data are.

Work was undertaken using a carefully selected study site soil (Stoke Bardolph). This site was selected for having sufficient concentration of trace metals and for observing the effects of long-term sewage sludge application. Thus this site was well suited to the analytical requirements, and furthering understanding of the effects of sewage sludge disposal to soil.

Pore water concentrations were interpreted in terms of both chemical concentration and predicted speciation. WHAM-VI was used as the most appropriate model, which confirmed the importance of organic complexation. In this way implications for bioavailability and dominant controls on solubility were drawn.

More detailed summaries are given below (section 7.1), with recommendations arising from this regard (section 7.2).

7.1. Key findings

Rhizon soil moisture samplers, centrifugation, high pressure squeezing and soil water suspensions were operationally tested as techniques for the recovery of pore water. Here the functionality, benefits and limitations of these methods are summarised.

7.1.1. Rhizon samplers

The overall geometric mean axial-radial influence of these samplers is very small, suggesting that careful consideration of the samplers' placement and experimental designs as a function of the characteristics of the soil under investigation is required. Rhizon samplers only function when the matric potential is greater than 10 kPa (above FC) otherwise the potential gradient and the hydraulic conductivity are too low to obtain a sample. Rhizon samplers appeared to sample water preferentially from the more accessible pool of water (extra-aggregate), when the studied soil was spiked with a known amount of ^{18}O labelled water. Furthermore, Rhizon samplers have been shown to be surface-coated with organic films following first-use in soils, raising the problem of possible adsorptions and/or chemical reactions on the surface. These films modifies their total porosity and, following acid washing, produce a protonated surface cation exchange capacity. This effect was especially reflected on the much lower concentrations observed for DOC and possibly some of the trace elements (V, Mn, Mo, Co, Ni and to a lesser extent Cr) compared to centrifugation and squeezing. The pH was also lower, which, in combination with the lower DOC, was causing a shift in the predicted speciation in favour of the free hydrated ions.

7.1.2. Centrifugation

Centrifugation extracts water from a wider range of pore sizes compared to Rhizon sampling, but nevertheless will still only yield a fraction of the total pore fluids (only a total efficiency of 28% was achieved). Compaction and pore size reduction occur during centrifugation. There is evidence to suggest that centrifugation was not able to differentiate between more and less accessible water at FC conditions (soil studied spiked with ^{18}O labelled water). During the process of centrifugation, the rate of mixing of the labelled water to the smaller pores is likely to increase dramatically by an apparent process of 'infusion'. This is reflected in the composition and speciation of the pore waters extracted, which is relatively homogeneous across the range of centrifugal speeds employed.

7.1.3. Squeezing

The rate of the pore water collected shows that sample texture and organic matter content are important variables to consider prior to extractions. The principal constraint of the methodology is the amount of time involved. Although rapid extractions at maximum pressure are possible, the aims of this project required slower, graded application of pressure. In this case a much longer duration, compared to centrifugation and Rhizon samplers, is required. The duration of the extraction constitutes a major limitation, especially when organic matter is a key component of the soil studied: decomposition of OM and anaerobism may lead to large variations in chemical composition and speciation. The closed system employed during soil squeezing generates time-dependent chemical (and redox) reactions within the solid-solution system: increasing reduction and pCO_2 during the later stage of squeezing extraction are evident. This was shown particularly by some of the main redox indicators such as NO_3^-, Mn and S, as well as the pH and alkalinity, the latter two rising during squeezing but remaining fairly constant during centrifugation.

7.1.4. Equilibrated electrolyte suspensions

Results showed that despite the large soil metal and OM concentrations, the soil studied demonstrated virtually no ability to buffer DOC and was only barely able to buffer the concentrations of the metal ions in pore water with increasing dilutions. Desorption of DOC is probably too slow to give a reliable or consistent value independent of soil:solution ratio (***R***)**.** On the other hand, there is good evidence that solubility/adsorption equilibria of free divalent metals were maintained (relatively constant $[M^{2+}]$ and very limited depletion of labile pool). The significance of this is that it is possible to attain a fairly reliable estimate of free metal ions (M^{2+}) even in strongly dilute suspension, but poor estimates of M_{soln} (e.g. for leaching studies) since they are highly dependent on operational aspects of the suspension/extraction scheme.

7.1.4. Chemistry and speciation of pore waters

Alkali and alkaline earth metals decreased in concentration with progressive extractions, both using centrifugation and squeezing at both temperatures. Very similar behaviour was shown by K, Na, Li, Ba, Ca, Mg and Sr in this respect.

Some transition metals showed to decrease in concentration (Pb, Al, Fe, Cd, Cu, Zn and Ni), some other seem to increase with progressive extractions (Mo, V, Co, Mn), whereas the remainder appear to have different behaviour between methods of extraction (Co, Cu, Cr).

Non-metallic elements, which include most of the anions, present contrasting behaviour. Some increased in concentration during squeezing (S, HCO_3, As, P, Br and to a lesser extent Si) but were fairly constant with progressive centrifugation. Others decreased with centrifugation (B, Cl, Si) or decreased during squeezing (NO_3).

Organic Carbon showed lower concentrations in samples withdrawn by Rhizon samplers compared to the other two methods, sometimes presenting better agreement with centrifugation data rather than with squeezing.

The pH was fairly constant during centrifugation whereas it increased in squeezed samples.

In general, the most important factors affecting pore water chemistry during extraction seem to be controlled by the conditions to which the samples are exposed during this process. For equal incubation time and conditions, the time employed for the pore water extractions and the environment in which soil samples lie (open and closed systems), may or may not trigger different chemical conditions, testified by changes in pH, alkalinity, redox potential and ultimately adsorption/desorption conditions during squeezing. However, the increasing pressure applied and the progressive decrease in ionic strength observed as well as decreasing in moisture content, do not rule out completely the possibility that less available water (thinner films around particles or intra-aggregate water) could be sampled during later stages of the squeezing extraction, therefore contributing to a set of different conditions of the solid-solution system. Solute isolation and differentiation within different pore classes as one of the possible causes of differences in chemistry during multiple pore water extractions, could be difficult to sustain from these results, unless corroborated by more evidence.

7.2. Final recommendations

- ***Rhizon samplers*** should be used as a disposable device, to avoid material modification with time, decrease in porosity and possibly significant variations in solute chemistry; this will inevitably increase the experimental costs in the case of larger designs.

- Results should be treated cautiously in cases where humic substances are present in the soil.
- They are only applicable for high moisture soil conditions, resulting in reduced applications to field or dryer conditions.
- No equipment required except syringes (or vacuum tubes), ease of handling/deployment and straightforward use constitute major advantages.
- No 'side-effects' (provided time is allowed for equilibration with the soil) if M^{2+} (free ion activity) were needed as opposed to M_{sol} (total metal in pore water), as often required in environmental studies.

- ***Centrifugation*** presents fewer material problems such as the coating happening for Rhizon samplers; however, tubes and other spare parts are not commercially available and often have to be built in-house.
- The method is optimal for bulk solution studies, or when homogenisation represents a key experimental point; targeted studies are also possible but would necessitate prior examination of the soil water holding capacity and release under varying centrifugal speeds, which could be demanding in terms of time and effort.

- ***Soil squeezing*** presents limitations in the case of a long duration extraction, therefore this should only be applied when OM is not a key factor.
- The method is not as accessible as the other three, at least with the present apparatus required, but there is space for further development and improvement (i.e. simplification of the design and/or reduction of labour required).
- Tests on 'fast' extractions with high initial pressures may produce good results and minimize the alterations produced by anaerobisms.

- ***Batch extractions*** are well suited for studies on M^{2+} activities, but more studies are needed to clarify the effect of ***R*** on metal and DOC solubility (buffer capacity)
- Suspensions with high solids concentrations should be used to approach more closely natural conditions, until more results are achieved to clarify the hysteresis of adsorption/desorption.

In summary, the importance of the method employed for soil pore water extraction should not be underestimated. Experimental design and performance should be chosen to reflect the particular aim of the study, reported in sufficient detail to allow others to make appropriate comparisons and the parameters operationally defined as a function of the method employed.

References

Abrahams, P.W. (2002). Soils: their implications to human health. *Science of the Total Environment*, **291(1-3)**, 1-32.

Adamo, P., Dudka, S., Wilson, M.J., and McHardy, W.J. (1996). Chemical and mineralogical forms of Cu an Ni in contaminated soils from the Subdury mining and smelting region, Canada. *Environmental Pollution*, **91(1)**, 11-19.

Adams, F., Burmester, C., Hue, N.V., and Long, F.L. (1980). Comparison of column-displacement and centrifuge methods for obtaining soil solution. *Soil Science of America Journal*, **44**, 733-735.

Aharoni, C., and Ungarish, M. (1977). Kinetics of activated chemisorption: part 3. Amount and distribution of adsorbate a varying temperatures and pressures. *Journal of the Chemical Society, Faraday Transactions I*, **73**, 1943-1950.

Albert, R.H., and Horwitz, W. (1995). Incomplete data sets: coping with inadequate databases. *Journal of AOAC International*, **78**.

Allison, J.D., Brown, D.S., and Novo-Gradac, K.J. (1991). MINTEQA2/PRODEFA2, a geochemical assessment model for environmental system. *EPA/600/3-91/021*, US Environmental Protection Agency, Athens, GA.

Alloway, B.J. (1995). *Heavy metals in soils*, Blackie Academic & Professional, an imprint of Chapman & Hall, London.

Amoozegar-Fard, A. D., Nielsen, D.R., and Warrick, A.W. (1982). Soil solute concentration distribution for spacially varying pore water velocities and apparent diffusion coefficients. *Soil Science Society of America Journal*, **46**, 3-9.

Andersen, M.K., Raulund-Rasmussen, K., Strobel, B.W., and Hansen, H.C.B. (2002). Adsorption of cadmium, copper, nickel, and zinc to a poly(tetrafluorethene) porous soil solution sampler. *Journal of Environmental Quality*, **31(1)**, 168-175.

Anderson, P.R., and Christensen, T.H. (1988). Distribution coefficients of Cd, Co, Ni, and Zn in soils. *Journal of Soil Science*, **39**, 15-22.

Antoniadis, V., and Alloway, B.J. (2002). Leaching of cadmium, nickel, and zinc down the profile of sewage sludge-treated soil. *Communications in Soil Science and Plant Analysis*, **33(1-2)**, 273-286.

Appelo, C.A.J., and Postma, D. (1994). *Geochemistry, Groundwater, and Pollution*, Rotterdam.

Áraguas-Áraguas, L., Rozanski, K., Gonfiantini, R., and Louvat, D. (1995). Isotope Effects Accompanying Vacuum Extraction of Soil-Water for Stable-Isotope Analyses. *Journal of Hydrology*, **168(1-4)**, 159-171.

Arnold, P.W. (1970). The behaviour of potassium in soils. *Fertil. Soc. Proc.*, **115**, 3-30.

Arnold, P.W. (1978). Surface-electrolyte interactions. In: *The chemistry of soil constituents*, Greenland, D.J., and Hayes, M.H.B., ed., Wiley, Chichester and New York.

Atanassova, I., and Okazaki, M. (1997). Adsorption-desorption characteristics of high levels of copper in soil clay fractions. *Water Air and Soil Pollution*, **98**, 213–228.

Atkins, P., and de Paula, J. (2001). *Physical Chemistry*, Oxford University Press, Oxford, 1180 p.

Baker, D.E., and Senft, J.P. (1995). Copper. In: *Heavy metals in soils*, B.J. Alloway, ed., Blackie Academic & Professional, an imprint of Chapman & Hall, London, 179-205.

Ball, J.W., Nordstrom, D.K., and Jenne, E.A. (1980). Additional and revised thermochemical data for WATEQ-2 computerized model for trace and major element speciation and mineral equilibria of natural waters. US Geological Survey Water Resource Investigations, Menlo Park, CA.

Barber, S.A. (1984). *Soil nutrient bioavailability: a mechanistic approach*, John Wiley, New York.

Barnes, C.J., and Turner, J.V. (1998). Isotopic exchange in soil water. In: *Isotope tracers in cachment hydrology*, C. Kendall, and McDonnell, J.J., ed., Elsevier, Amsterdam, 137-162.

Barrow, N.J. (1986). Testing a mechanistic model:II. The effects of time and temperature on the reaction of zinc with a soil. *Journal of Soil Science*, **37**, 277-286.

Bartlett, R.J., and James, B.R. (1988). Chapter 10. In: *Chromium in the natural and human environment*, J.O. Nriagu, and Nieboer, E., ed., John Wiley, New York.

Bascomb, C.L. (1964). Rapid method for the determination of cation exchange capacity of calcareous and non-calcareous soils. *Journal of the Science of Food and Agriculture*, **15**, 821-823.

Basta, N.T., and Tabatabai, M.A. (1992). Effect of cropping systems on adsorption of metals by soils. II. Effect of pH. *Soil Science*, **153**, 195-204.

Batley, G.E., and Giles, M.S. (1979). Solvent displacement of sediment interstitial waters before trace-metal analysis. *Water Research*, **13(9)**, 879-886.

Beckman Coulter Instruments, (2003). Technical Application Information Bulletins - 403. Particle Size Analysis - Evaluating Laser Diffraction Systems in the light of ISO 13320-1, I. Ley, ed., Beckman Coulter UK Ltd, Oakley Court, Kingsmead Business Park, London Road, High Wycombe, HP11 1JU, Bucks, UK, 11, available online at the URL: http://www.beckmancoulter.com/Literature/BioResearch/ta-403.pdf

Beckman Instruments, (1988). Instructions for using the JA-10 fixed angle rotor. Beckman J-21 Series, J-6, and J-6B, Spinco Division of Beckman Instruments, INC., Palo Alto, Ca.

Behel, D., Nelson, D.W., and Sommers, L.E. (1983). Assessment of heavy-metal equilibria in sewage sludge-treated Soil. *Journal of Environmental Quality*, **12(2)**, 181-186.

Beier, C., and K. Hansen. (1992). Evaluation of porous cup soil-water samplers under controlled field conditions: comparison of ceramic and PTFE cups. *Journal of Soil Science*, **43**, 261-271.

Beier, C., Hansen, K., Gundersen, P., and Andersen, B.R. (1992). Long-term field comparison of ceramic and poly(tetrafluoroethene) porous cup soil water samplers. *Environmental Science Technology*, **26**, 2005-2011.

Belzile, N., Chen, Y., and Wang, Z. (2001). Oxidation of antimony III by amorphous iron andmanganese oxyhydroxides. *Chemical Geology*, **174**, 379-387.

Benedetti, M.F., VanRiemsdijk, W.H., Koopal, L.K., Kinniburgh, D.G., Gooddy, D.C., and Milne, C.J. (1996a). Metal ion binding by natural organic matter: From the model to the field. *Geochimica et Cosmochimica Acta*, **60(14)**, 2503-2513.

Benedetti, M.F., VanRiemsdik, W.H., and Koopal, L.K. (1996b). Humic substances considered as a heterogeneous donnan gel phase. *Environmental Science & Technology*, **30(6)**, 1805-1813.

Bethke, C.M. (1996). *Geochemical Reaction Modeling*, Oxford University Press, New York.

Beven, K. (1989). Changing ideas in hydrology - the case of physically-based models. *Journal of Hydrology*, **105(1-2)**, 157-172.

Beven, K., and Germann, P.F. (1982). Macropores and water flow in soils. *Water Resources Research*, **18**, 1311-1325.

Bidwell, A.M., and Dowdy, R.H. (1987). Cadmium and zinc availability to corn following termination of sewage sludge applications. *Journal of Environmental Quality*, **16**, 438/442.

Biggar, J.W., and Nielsen, D.R. (1976). Spatial variability of leaching characteristics of a field soil. *Water Resources Research*, **12(1)**, 78-84.

Blake, G.R., and Hartge, K.H. (1986). Bulk density. In: *Methods of soil analysis, Part 1. Physical and mineralogical methods*, A. Klute, ed., American Society of Agronomy - Soil Science Society of America, Madison, WI, 363-375.

Boekhold, A.E., Temminghoff, E.J.M., and Vanderzee, S.E.A.T.M. (1993). Influence of electrolyte composition and pH on cadmium sorption by an acid sandy soil. *Journal of Soil Science*, **44**, 85-96.

Boggess, W.R. (1977). Summary and conclusions. In: *Lead in the environment*, National Science Foundation, Washington, DC, 267-272.

Bohn, H., McNeal, B., and O'Connor, G. (1985). *Soil Chemistry*, 2nd edition, John Wiley & Sons, New York, 341 p.

Bolt, G.H., De Boodt, M.F., Hayes, M.H.B., and McBride, M.B. (1991). *Interactions at the Soil Colloid-Soil Solution Interface*, Kluwer Academic Publishers, Dordrecht.

Booltink, H.W.G., and Bouma, J. (1991). Morphological characterization of bypass flow in well-structured clay soil. *Soil Science Society of America Journal*, **55**, 1249-1254.

Bordas, F., and Bourg, A. (2001). Effect of solid/liquid ratio on the remobilization of Cu, Pb, Cd and Zn from polluted river sediment. *Water Air and Soil Pollution*, **128(3-4)**, 391-400.

Bordas, F., and Bourg, A.C.M. (1998). A critical evaluation of sample pretreatment for storage of contaminated sediments to be investigated for the potential mobility of their heavy metal load. *Water Air and Soil Pollution*, **103(1-4)**, 137-149.

Borkovec, M., and Westall, J. (1983). Solution of the Poisson-Boltzmann equation for surface excesses of ions in the diffuse layer at the oxide-electrolyte interface. *Journal of Electroanalytical Chemistry*, **150**, 325-337.

Børretzen, P., and Salbu, B. (2004). Geochemical models for sediment-seawater interactions. Laboratory for Analytical Chemistry Institute for Chemistry and Biotechnology; Agricultural University of Norway, 1432

Ås, Norway. URL: http://npolar.no/transeff/Transport/Pollution/Progress/Borretzen_Salbu_GeochModels.doc

Brady, N. C., and Weil, R.R. (1999). *The nature and properties of soils*, Prentice-Hall, Upper Saddle River, New Jersey.

Bresler, E. (1978). Analysis of trickle irrigation with application to design problems. *Irrigation Science*, **1**, 3-17.

Brewer, R. (1964). *Fabric and mineral analysis of soil*, J. Wiley, New York.

Briggs, D., and Seah, M.P. (1990). *Auger and X-ray Photoelectron Spectroscopy. Practical Surface Analysis*, Wiley, Chichester, UK.

Brightman, M.A., Bath, A.H., Cave, M.R., and Darling, W.G. (1985). Pore fluids from the argillaceous rocks of the Harwell region. *85-6*, British Geological Survey, Keyworth, Nottingham.

Broadbent, F. E. (1953). The soil organic fraction. *Advances in Agronomy*, **5**, 153-183.

Bufflap, S.E., and Allen, H.E. (1995a). Sediment pore water collection methods for trace metals analysis: a review. *Water Research*, **29(1)**, 165-177.

Bufflap, S.E., and Allen, H.E. (1995b). Comparison of pore water sampling techniques for trace metals. *Water Research*, **29(9)**, 2051-2054.

Bullock, P., and Thomasson, A.J. (1979). Rothamsted studies of soil structure, 2. Measurement and characterization of macroporosity by image analysis and comparison with data from water retention measurements. *Journal of Soil Science*, **30(3)**, 391-414.

Burgess, P.S. (1922). The soil solution, extracted by Lipman's direct-pressure method, compared with 1:5 water extracts. *Soil Science*, **14**, 191-216.

Cabrera, R.I. (1998). Monitoring chemical properties of container growing media with small soil solution samplers. *Scientia Horticulturae*, **75**, 113-119.

Cameron, F.K. (1911). *The soil solution: the nutrient medium for plant growth*, Chemical Publishing, Easton, PA.

Cances, B., Ponthieu, M., Castrec-Rouelle, M., Aubry, E., and Benedetti, M.F. (2003). Metal ions speciation in a soil and its solution: experimental data and model results. *Geoderma*, **113(3-4)**, 341-355.

Candelaria, L.M., and Chang, A.C. (1997). Cadmium activities, solution speciation, and solid phase distribution of Cd in cadmium nitrate and sewage sludge-treated soil systems. *Soil Science*, **162(10)**, 722-732.

Carbonell-Barrachina, A., Jugsujinda, A., DeLaune, R. D., Patrick, W. H., Burlo, F., Sirisukhodom, S., and Anurakpongsatorn, P. (1999). The influence of redox chemistry and pH on chemically active forms of arsenic in sewage sludge-amended soil. *Environment International*, **25(5)**, 613-618.

Cavallaro, N., and McBride, M.B. (1980). Activities of Cu^{2+} and Cd^{2+} in soil solutions as affected by pH. *Soil Science Society of America Journal*, **44**, 729-732.

Cavallaro, N., and McBride, M.B. (1984). Zinc and copper sorption and fixation by an acid soil clay: effect of selective dissolutions. *Soil Science Society of America Journal*, **48**, 1050-1054.

Cave, M.R., Reeder, S., Entwisle, D.C., Blackwell, P.A., Trick, J.K., Wragg, J., and Burden, S.R. (1998). Extraction and analysis of pore waters from bentonite clay. *WI/98/9C*, British Geological Survey, Keyworth, Nottingham.

Celardin, F. (1999). Semi-empirical correlations between so-called mobilizable and mobile concentrations of heavy metals in soils. *Communications in Soil Science and Plant Analysis*, **30(5-6)**, 843-854.

Celorie, J.A., Woods, S.L., Vinson, T. S., and Istok, J. D. (1989). A comparison of sorption equilibrium distribution coefficients using batch and centrifugation methods. *Journal of Environmental Quality*, **18(3)**, 307-313.

Cernik, M., Federer, P., Borkovec, M., and Sticher, H. (1994). Modeling of heavy metal transport in a contaminated soil. *Journal of Environmental Quality*, **23**, 1239–1248.

Chapman, P.J., Edwards, A.C., and Shand, C.A. (1997a). The phosphorus composition of soil solutions and soil leachates: influence of soil:solution ratio. *European Journal of Soil Science*, **48**, 703-710.

Chapman, P.J., Shand, C.A., Edwards, A.C., and Smith, S. (1997b). Effect of storage and sieving on the phosphorus composition of soil solution. *Soil Science Society of America Journal*, **61(1)**, 315-321.

Chen, Y. W., Deng, T.L., Filella M., and Belzile N. (2003). Distribution and early diagenesis of antimony species in sediments and porewaters of freshwater lakes. *Environmental Science & Technology*, **37(6)**, 1163-1168.

Cheshire, M.V., Berrow, M.L., Goodman, B.A., and Mundie, C.M. (1977). Metal Distribution and Nature of Some Cu, Mn and V Complexes in

Humic and Fulvic-Acid Fractions of Soil Organic-Matter. *Geochimica Et Cosmochimica Acta*, **41(8)**, 1131-1138.

Coats, K.H., and Smith, B.D. (1964). Dead-end pore volume and dispersion in porous media. *Society of Petroleum Engineers Journal*, **4(1)**, 73-84.

Conca, J.L., and Wright, J.V. (1990). Diffusion coefficients in gravel under unsaturated conditions. *Water Resources Research*, **26**, 1055-1066.

Conca, J.L., and Wright, J.V. (1992). Flow and diffusion in unsaturated gravel, soil and whole rock. *Applied Hydrogeology*, **1**, 5-24.

Cook, R.L., and Langford, C.H. (1998). Structural characterization of a fulvic acid and a humic acid using solid state ramp-CP-MAS C-13 nuclear magnetic resonance. *Environmental Science and Technology*, **32**, 719–725.

Coplen, T.B., Herczeg, A.L., and Barnes, C. (1999). Isotope engineering - Using stable isotopes of the water molecule to solve practical problems. In: *Environmental tracers in subsurface hydrology*, R. Cook, and Herczeg, A.L., ed., Kluwer Academic Press, Boston, 79-110.

Courchesne, F., Turmel, M.C., and Beauchemin, P. (1996). Magnesium and potassium release by weathering in Spodosols: grain surface coating effects. *Soil Science Society of America Journal*, **60**, 1188-1196.

Cozzarelli, I. M., Herman, J. S., and Parnell, R. A. (1987). The Mobilization of Aluminum in a Natural Soil System - Effects of Hydrologic Pathways. *Water Resources Research*, **23(5)**, 859-874.

Crawford, M.B. (1996). PHREEQEV: the incorporation of a version of Model V for organic complexation in aqueous solution into the speciation code PHREEQE. *Computers & Geosciences*, **22(2)**, 109-116.

Crecelius, E.A., Johnson, C.J., and Hofer, G.C. (1974). Contamination of soils near a copper smelter by arsenic, antimony and lead. *Water, Air and Soil Pollution*, **3**, 337–342.

Criss, R.E. (1999). *Principles of stable isotope distribution*, Oxford University Press, New York.

Curtin, D., and Smillie, G.W. (1995). Effect of incubation and pH on soil solution and exchangeable cation ratios. *Soil Science Society of America Journal*, **59**, 1006-1011.

Dahlgren, R.A. (1993). Comparison of soil solution extraction procedures: effect on solute chemistry. *Communications in Soil Science and Plant Analysis*, **24(15-15)**, 1783-1794.

Dallavalle, J.M. (1948). *Micromeritics: the technology of fine particles*, Pitman, New York.

Darling, W.G., and Bath, A.H. (1988). A stable isotope study of recharge processes in the English Chalk. *Journal of Hydrology*, **101(1-4)**, 31-46.

Davies, B.E., and Davies, R.I. (1963). A simple centrifugation method for obtaining small samples of soil solution. *Nature*, **198**, 216-217.

Davis, J.A., and Kent, D.B. (1990). Surface complexation modeling in aqueous geochemistry. In: *Mineral-Water Interface Geochemistry*, M.F. Hochella, and White, A.F., ed., Mineralogical Society of America, Washington D.C., 177-260.

Davranche, M., and Bollinger, J.C. (2001). A desorption-dissolution model for metal release from polluted soil under reductive conditions. *Journal of Environmental Quality*, **30(5)**, 1581-1586.

Davranche, M., Bollinger, J.C., and Bril, H. (2003). Effect of reductive conditions on metal mobility from wasteland solids: an example from the Mortagne-du-Nord site (France). *Applied Geochemistry*, **18(3)**, 383-394.

De Coninck, F. (1980). Major mechanisms in formation of spodic horizons. *Geoderma*, **24**, 101-128.

Degryse, F., Broos, K., Smolders, E., and Merckx, R. (2003). Soil solution concentration of Cd and Zn can be predicted with a $CaCl_2$ soil extract. *European Journal of Soil Science*, **54(1)**, 149-157.

Dengis, P.B., Gerin, P.A., and Rouxhet, P.G. (1995). X-Ray Photoelectron-Spectroscopy analysis of biosurfaces - Examination of performances with yeast-cells and related model compounds. *Colloids and Surfaces B-Biointerfaces*, **4(4)**, 199-211.

DETR. (1999). Draft waste strategy for England and Wales. *99EP0254*, DETR.

Di Toro, D.M. (1985). A particle interaction model of reversible organic chemical sorption. *Chemosphere*, **14**, 1503-1538.

DoE, (1993). UK sewage sludge survey. Final report. Department of Environment, Consultants in Environmental Sciences Ltd, Gateshead.

DoE, (1996). Code of practice for agricultural use of sewage sludge. *(ISBN 185112005)*, Department of Environment, Goldthorpe, Rotherham, UK.

Domenico, P.A., and Schwartz, F.W. (1990). *Physical and chemical hydrology*, Wiley & Son, New York.

Drever, J.I. (1982). *The Geochemistry of Natural Waters*, Prentice-Hall, Englwood Cliffs.

Driscoll, C.T., Fuller, R.D., and Simone, D.M. (1988). Longitudinal variations in trace metal concentrations in a northern forested ecosystem. *Journal of Environmental Quality*, **17**, 101-107.

Driscoll, C.T., Otton, J.K., and Iverfeldt, Å. (1994). Trace metals speciation and cycling. In: *Biogeochemistry of small cachments - A tool for environmental research*, M. Bedrich, and Černý, J., ed., Wiley & Sons, Prague; available on internet at the URL: www.icsu-scope.org/downloadpubs/scope51/

Dudka, S., Ponce-Hernandez, R., Tate, G., Hutchinson, T.C. (1996). Forms of Cu, Ni and Zn in soils of Subdury, Ontario and the metal concentrations in plants. *Water, Air and Soil Pollution*, **90**, 531-542.

Dumestre, A., Sauve, S., McBride, M., Baveye, P., and Berthelin, J. (1999). Copper speciation and microbial activity in long-term contaminated soils. *Archives of Environmental Contamination and Toxicology*, **36(2)**, 124-131.

Dzombak, D. A., and Morel, F.M.M. (1990). *Surface complexation modeling-Hydrous ferric oxide*, John Wiley, New York.

Dzombak, D.A., and Morel, F.M.M. (1987). Adsorption of inorganic pollutants in aquatic systems. *Journal of Hydraulic Engineering-Asce*, **113(4)**, 430-475.

Environment Agency, (2001). CEC and K_d Determination in Landfill Performance Evaluation. A review of methodologies and preparation of standard materials for laboratory analysis. *P1/254/01*, Environment Agency.

EC, (1986). Council Directive 86/278/EEC of 12 June 1986 on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture. *Official Journal of the European Communities,* **181**, 6 -12.

EC, (1991). Council Directive 91/271/EEC of 21 May 1991 concerning urban waste-water treatment. *Official Journal of the European Communities*, **135**, 40 -52.

EC, (1998). Mis en oeuvre de la directive 91/271/ CEE du Conseil du 21 mai 1991 relative au traitement des eaux urbaines résiduaires, modifiée par la directive 98/15/CE de la commission du 27 février 1998. *98/15/CE*, European Commission.

EC, (2000a). Report from the Commission to the Council and the European Parliament on the implementation of Community Waste Legislation Directive 75/442/EEC on waste, Directive 91/689/EEC on hazardous

waste, Directive 75/439/EEC on waste oils and Directive 86/278/EEC on sewage sludge for the period 1995–1997. European Commission, Bruxelles.

EC, (2000b). Working document on sludge, 3rd draft. *ENV.E3/LM*, European Commission, Bruxelles.

EC, (2000c). Working document. Biological treatment of biodegradable waste on sludge, first draft. European Commission, Bruxelles.

Edmunds, W. M., and Bath, A.H. (1976). Centrifuge extraction and chemical analysis of interstitial waters. *Environmental Science Technology*, **10**, 467-472.

Edwards, R., Lepp, N.W., and Jones, K.C. (1995). Other less abundant elements of potential environmental significance. In: *Heavy metals in soils*, B. J. Alloway, ed., Blackie Academic & Professional, London, 306-352.

Elliot, H.A., Liberati, M.R., and Huang, C.P. (1986). Competitive adsorption of heavy metals by soils. *Journal of Environmental Quality*, **15**, 214-219.

Elrashidi, M.A., and O'Connor, G.A. (1982). Influence of solution composition on sorption of zinc by soils. *Soil Science Society of America Journal*, **46**, 1153–1158.

England, C.B. (1974). Comments on A technique using porous cup for water sampling at any depth in the unsaturated zone by W.W. Wood. *Water Resources Research*, **10**, 1049.

Entwisle, D.C., and Reeder, S. (1993). New apparatus for pore fluid extraction from mudrocks for geochemical analysis. In: *Geochemistry of Clay-Pore Fluid Interaction*, D. A. C. Manning, Hall, P.L. and Hughes, C.R., ed., Chapman & Hall, London, 365-388.

Epstein, S., and Mayeda, T.K. (1953). Variation of ^{18}O content of waters from natural sources. *Geochimica et Cosmochimica Acta*, **4**, 213-224.

Eriksson, J. (2001). Concentrations of 61 trace elements in sewage sludge, farmyard manure, mineral fertiliser, precipitation and in oil and crops. *5159*, Swedish Environmental Protection Agency, Uppsala, Sweden; available on internet at the URL: www.naturardsverket.se/pdf/620-6246-8.pdf.

Essert, S., and J.W. Hopmans. (1998). Combined tensiometer-solution sampling probe. *Soil & Tillage Research*, **45**, 299-309.

Essington, M.E., and Mattigod, S.V. (1991). Trace-Element Solid-Phase Associations in Sewage-Sludge and Sludge-Amended Soil. *Soil Science Society of America Journal*, **55(2)**, 350-356.

Evans, L.J. (1989). Chemistry of metal retention by soils. *Environmental Science & Technology*, **23**, 1046-1056.

Förstner, U. (1991). Soil pollution phenomena - Mobility of heavy metals in contaminated soil. In: *Interactions at the soil colloid-soil solution interface*, G.H. Bolt, De Boodt, M.F., Hayes, M.H.B., and McBride, M.B., ed., Kluwer Academic Publisher, Dordrecht, Nederlands, 543-582.

Fotovat, A., Naidu, R., and Sumner, M. (1997). Water:soil ratio influences aqueous phase chemistry of indigenous copper and zinc in soils. *Australian Journal of Soil Research*, **35**, 687-709.

Mason, B., and Berry, L.G. (1968). *Elements of Mineralogy*, Freeman, W.H., New York.

Freeze, R.A., and Cherry, J.A. (1979). *Groundwater*, Prentice-Hall, Englewood Cliffs, NJ.

Friedland, A.J., and Johnson, A.H. (1985). Lead distribution of fluxes in a high-elevation forest in northern Vermont. *Journal of Environmental Quality*, **14**, 332-336.

FWR. (1999). UK Sewage Sludge Survey 1996-97. WRc, Medmenham, England.

Gabriel, P. (1982). San Jacinto. In: Security.

Gamerdinger, A.P., and Kaplan, D.I. (2000). Application of a continuous-flow centrifugation method for solute transport in disturbed, unsaturated sediments and illustration of mobile-immobile water. *Water Resources Research*, **36(7)**, 1747-1755.

Gao, S.A., Walker, W.J., Dahlgren, R.A., and Bold, J. (1998). Simultaneous sorption of Cd, Cu, Ni, Zn, Pb, and Cr on soils treated with sewage sludge supernatant. *Water Air and Soil Pollution*, **93**, 331–345.

Garcia-Miragaya, J. (1984). Levels, chemical fractionation, and solubility of lead in roadside soils of Caracas, Venezuela. *Soil Science*, **138**, 147-152.

Gardiner, T. M., Miller, R.W., Badamchian, B., Azzari, A.S., and Sissin, D.R. (1995). Effects of repeated sewage sludge applications on plant accumulation of heavy metals. *Agriculture Ecosystems and Environment*, **55 (1)**, 1-6.

Gaudet, J.P., Jegat, H., Vachaud, G., and Wierenga, P.J. (1977). Solute transfer, with exchange between mobile and stagnant water, through unsaturated sand. *Soil Science Society of America Journal*, **41(4)**, 665-671.

Gazis, C., and Feng, X.H. (2004). A stable isotope study of soil water: evidence for mixing and preferential flow paths. *Geoderma*, **119(1-2)**, 97-111.

Gendebien, A., Carlton-Smith, C., Izzo, M., and Hall, J.E. (1999). UK Sewage sludge survey - National presentation. *P 165*, Environment Agency (England and Wales).

GenStat® Release 7.1, Part 2: Statistics, (2003). Lawes Agricultural Trust (Rothamsted Experimental Station). R.W. Payne, ed., VSN International, Wilkinson House, Jordan Hill Road, Oxford, UK.

Gerin, P.A., Dengis, P.B., and Rouxhet, P.G. (1995). Performance of XPS analysis of model biochemical-compounds. *Journal De Chimie Physique et de Physico-Chimie Biologique*, **92(5)**, 1043-1065.

Gerin, P.A., Genet, M.J., Herbillon, A.J., and Delvaux, B. (2003). Surface analysis of soil material by X-ray photoelectron spectroscopy. *European Journal of Soil Science*, **54**, 589–603.

Gerritse, R.G., Adeney, J.A., Baird, G., and Colquhoun, I. (1992). The reaction of copper ions and hypochlorite with minesite soils in relation to fungicidal activity. *Australian Journal of Soil Research*, **30(5)**, 723-735.

Gerritse, R.G., and Vandriel, W. (1984). The relationship between adsorption of trace metals, organic matter, and pH in temperate soils. *Journal of Environmental Quality*, **13(2)**, 197-204.

Gier, S., and Johns, W.D. (2000). Heavy metal-adsorption on micas and clays minerals sudied by X-ray photoelectron spectroscopy. *Applied Clay Science*, **16**, 289-299.

Giesler, R., Lundstrom, U.S., and Grip, H. (1996). Comparison of soil solution chemistry assessment using zero- tension lysimeters or centrifugation. *European Journal of Soil Science*, **47(3)**, 395-405.

Gooddy, D.C., Shand, P., Kinnigurgh, D.G., and Van Riemsdijk, W.H. (1995). Field-based partition coefficients for trace elements in soil solutions. *European Journal of Soil Science*, **46**, 265-285.

Gosz, J.R., Likens, G.E., and Bonnann, F.H. (1976). Organic matter and nutrient dynamics of the forest floor in the Hubbard Brook Forest. *Oecologia (Berlin)*, **22**, 305-320.

Goyne, K.W., Day, R.L., and Chorover, J. (2000). Artifacts caused by collection of soil solution with passive capillary samplers. *Soil Science Society of America Journal*, **64(4)**, 1330-1336.

Gray, C.W., and McLaren, R.G. (2003). Effects of air drying or sample storage on soil-solution properties of biosolids-amended soil. *Communications in Soil Science and Plant Analysis*, **34(15-16)**, 2327-2338.

Gray, C.W., McLaren, R.G., Roberts, A.H.C., and Condron, L.M. (1999). Solubility, sorption and desorption of native and added cadmium in relation to properties of soils in New Zealand. *European Journal of Soil Science*, **50**, 127–137.

Green, C. H., Heil, D. M., Cardon, G.E., Butters, G.L., and Kelly, E.F. (2003). Solubilization of manganese and trace metals in soils affected by acid mine runoff. *Journal of Environmental Quality*, **32(4)**, 1323-1334.

Greenland, D. J. (1981). Soil management and soil degradation. *Journal of Soil Science*, **32(3)**, 301-306.

Greenland, D.J. (1971). Interactions between humic and fulvic acids and clay. *Soil Science*, **111**, 34-41.

Greenland, D.J., and Hayes, M.H.B. (1981). *The chemistry of soil processes*, John Wiley & Sons, Chichester.

Gregson, K., Hector, D.J., and McGowan, M. (1987). A One-Parameter Model for the Soil-Water Characteristic. *Journal of Soil Science*, **38(3)**, 483-486.

Grieve, I.C. (1996). Effects of the centriguge drainage method on the total organic carbon concentrations in soil solutions from peaty soils. *Geoderma*, **74**, 115-123.

Grossmann, J., and Udluft, P. (1991). The extraction of soil water by the suction-cup method: a review. *Journal of Soil Science*, **42**, 83-93.

Grossmann, J., Bredemeier, M., and Udluft, P. (1990). Sorption of trace metals by suction cups. *Zeitschrift fur Pflanzenernahhrung und Bodenkunde*, **153**, 359-364.

Grove, J.H., and Ellis, B.G. (1980). Extractable chromium as related to soil pH and applied chromium. *Soil Science Society of America Journal*, **44**, 238-242.

Grover, R., and Hance, R.J. (1970). Effect of ratio of soil to water on adsorption of linuron and atrazine. *Soil Science*, **100**, 136-138.

Gu, B.H., Schmitt, J., Chen, Z., Liang, L.Y., and McCarthy, J.F. (1994). Adsorption and desorption of natural organic matter on iron oxide - mechanisms and models. *Environmental Science & Technology*, **28**, 38-46.

Guggenberger, G., and Zech, W. (1992). Sorption of dissolved organic-carbon by ceramic P-80 suction cups. *Zeitschrift Fur Pflanzenernahrung Und Bodenkunde*, **155(2)**, 151-155.

Gupta, U.C. (1971). Influence of Various Organic Materials on Recovery of Molybdenum and Copper Added to a Sandy Clay Loam Soil. *Plant and Soil*, **34(1)**, 249.

Gvirtzman, H., and Gorelick, S.M. (1991). Dispersion and advection in unsaturated porous media enhanced by anion exclusion. *Nature*, **352**, 793 - 795.

Haines, B.L., Waide, J.B., and Todd, R.L. (1982). Soil solution nutrient concentrations sampled with tension and zero-tension lysimeters: report of discrepancies. *Soil Science Society of America Journal*, **46**, 658-661.

Hamon, R.E., Holm, P.E., Lorenz, S.E., McGrath, S.P., and Christensen, T.H. (1999). Metal uptake by plants from sludge-amended soils: caution is required in the plateau interpretation. *Plant and Soil*, **216**, 53-64.

Hani, H. (1996). Soil analysis as a tool to predict effects on the environment. *Communications in Soil Science and Plant Analysis*, **27(3-4)**, 289-306.

Hansen, E.A., and Harris, A.R. (1975). Validity of soil-water samples collected with porous ceramics cups. *Soil Science Society of America Journal*, **39**, 528-536.

Hart, G.L., and Lowery, B. (1997). Axial-radial influence of porous cup soil solution samplers in a sandy soil. *Soil Science Society of America Journal*, **61(6)**, 1765-1773.

Hart, G.L., Lowery, B., McSweeney, K., and Fermanich, K.J. (1994). In situ characterization of hydrologic properties of Sparta sand: relation to solute travel using time domain reflectometry. *Geoderma*, **64**, 41-55.

Harter, R.D. (1983). Effect of soil pH on adsorption of lead, copper, zinc, and nickel. *Soil Science Society of America Journal*, **47(1)**, 47-51.

Harter, R.D. (1992). Competitive corption of cobalt, copper, and nickel ions by a calcium-saturated soil. *Soil Science Society of America Journal*, **56(2)**, 444-449.

Harter, R.D., and Naidu, R. (2001). An assessment of environmental and solution parameter impact on trace-metal sorption by soils. *Soil Science Society of America Journal*, **65(3)**, 597-612.

Harvey, J.W. (1993). Measurement of variation in soil solute tracer concentration across a range of effective pore size. *Water Resources Research*, **29(6)**, 1831-1837.

Hastings, D.W., Emeerson, S.R., Erez, J., and Nelson, B.K. (1996). Vanadium in foraminiferal calcite: Evaluation of a method to determine paleo-seawater vanadium concentrations. *Geochimica Et Cosmochimica Acta*, **60**, 3701-3715.

Haworth, A. (1990). A review of the modelling of sorption from aqueous-solution. *Advances in Colloid and Interface Science*, **32(1)**, 43-78.

Hayes, M.H.B. (1985). Extraction of humic substances from soil. In: *Humic substances in soil, sediment, and water*, G. Aiken, McKnight, D.M., Wershaw, R.L., and MacCarthy, P., ed., John Wiley & Sons, New York, 329-386.

Head, K.H. (1992). Density and particle density - Particle size. In: *Manual of soil laboratory testing - Soil classification and compaction tests*, Pentech Press, London, 116-234.

Heaven, F.W., and Delve, M. (1997). Detailed investigation of heavy metal and agricultural nutrient content of soils. *352/1*, Land Research associates, Lockington Hall, Lockington, Derby.

Hem, J.D. (1989). Study and interpretation of the chemical characteristics of natural water. *2254*, U.S. Geological Survey, Alexandria, VA.

Hesterberg, D. (1998). Biogeochemical cycles and processes leading to changes in mobility of chemical in soils. *Agriculture, Ecosystems & Environment*, **67,** 121-133.

Hillel, D. (1982). *Introduction to soil physics*, Academic Press, London.

Hillier, S., Suzuki, K., and Cotter-Howells, J. (2001). Quantitative determination of Cerussite (lead carbonate) by X-ray powder diffraction and inferences for lead speciation and transport in stream sediments from a former lead mining area of Scotland. *Applied Geochemistry*, **16**, 597-608.

HMSO, (1989). Sludge (Use in Agriculture) Regulations 1989 (SI 1989 No. 1790), amended 1990 (SI 1990 No. 880), available online: http://www.legislation.hmso.gov.uk/si/si1989/Uksi_19891263_en_1.htm

Hoefs, J. (1996). *Stable isotope geochemistry*, Springer-Verlag, Berlin.

Hooda, P.S., McNulty, D., Alloway, B.J., and Aitken, M.N. (1997). Plant availability of heavy metals in soils previously amended with heavy applications of sewage sludge. *Journal of the Science of Food amd Agricculture*, **73**, 446-454.

Hooda, P.S., Zhang, H., Davison, W., and Edwards, A.C. (1999). Measuring bioavailable trace metals by diffusive gradients in thin films (DGT): soil moisture effects on its performance in soils. *European Journal of Soil Science*, **50(2)**, 285-294.

Horita, J., and Wesolowski, D.J. (1994). Liquid-vapor fractionation of oxygen and hidrogen isotopes of water from the freezing to the critical temperature. *Geochimica et Cosmochimica Acta*, **58**, 3425-3437.

Horn, A.L., During, R.A., and Gath, S. (2003). Comparison of decision support systems for an optimised application of compost and sewage sludge on agricultural land based on heavy metal accumulation in soil. *Science of the Total Environment*, **311(1-3)**, 35-48.

Horseman, S.T., Higgo, J.J.W., Alexander, J., and Harrington, J.F. (1996). Water, gas and solute movement through argillaceous media. *CC-96/1*, Nuclear Energy Agency (NEA), Paris.

Hough, R.L., Young, S.D., and Crout, N.M.J. (2003). Modelling of Cd, Cu, Ni, Pb and Zn uptake, by winter wheat and forage maize, from a sewage disposal farm. *Soil Use and Management*, **19(1)**, 19-27.

Huber, C., Filella, M., and Town, R. M. (2002). Computer modelling of trace metal ion speciation: practical implementation of a linear continuous function for complexation by natural organic matter. *Computers & Geosciences*, **28(5)**, 587-596.

Hudson, B.D. (1994). Soil organic matter and available water capacity. *Journal of Soil and Water Conservation*, **49**, 189-194.

Hyun, H., Chang, A.C., Parker, D.R., and Page, A.L. (1998). Cadmium solubility and phytoavailability in sludge-treated soil: Effects of soil organic carbon. *Journal of Environmental Quality*, **27(2)**, 329-334.

Impellitteri, C.A., Allen, H.E., Yin, Y., You, S., and Saxe, J.K. (2001). Soil properties controlling metal partitioning. In: *Heavy metals release in soils*, H. M. Selim, and Sparks, D.L., ed., CRC Press LLC, Lewis Publishers, Boca Raton, Florida, 149-165.

Impellitteri, C.A., Saxe, J.K., Cochran, M., Janssen, G., and Allen, H.E. (2003). Predicting the bioavailability of copper and zinc in soils: Modeling the

partitioning of potentially bioavailable copper and zinc from soil solid to soil solution. *Environmental Toxicology and Chemistry*, **22(6)**, 1380-1386.

Ingham, M.N., and Vrebos, B.A.R. (1994). High productivity XRF analysis. *Advances in X-ray Analysis*, **37**, 717-724.

ISO, (1998). Soil quality - Determination of the water-retention characteristic - Laboratory methods. BS 7755-5.5:1999, Technical Committee ISO/TC 190, BSI, London, 389 Chiswick High Road, W4 4AL.

ISO, (1999). 13320-1: Particle size analysis - LASER diffraction methods - Part 1: General principles. Technical Committee TC 24/SC 4, International Organization for Standardization, Geneve, 34.

IUPAC, (2001). Appendix II. Definitions, Terminology and Symbols in Colloid and Surface Chemistry, part I. *57*, International Union of Pure and Applied Chemistry, Commission on Colloid and Surface Chemistry Including Catalysis, Washington, DC; available on internet at the URL: http://www.iupac.org/reports/2001/colloid_2001/manual_of_s_and_t.pdf

James, B.R., and Bartlett, R.J. (1983). Behavior of chromium in soils. VI. Interactions between oxidation-reduction and organic complexation. *Journal of Environmental Quality*, **12**, 173–176.

Janssen, C.R., Heijerick, D.G., De Schamphelaere, K.A.C., and Allen, H.E. (2003). Environmental risk assessment of metals: tools for incorporating bioavailability. *Environment International*, **28(8)**, 793-800.

Jardine, P.M., Wilson, G.V., and Luxmore, R.J. (1990). Unsaturated solute transport through a forest soil during rain storm events. *Geoderma*, **46**, 103-118.

Jenne, E.A. (1968). Controls on Mn, Fe, Co, Ni, Cu, and Zi concentrations in soils and water: the significant role of hydrous Mn and Fe oxides. *Advances in Chemical Ser.*, **73**, 337-387.

Jenne, E.A. (1977). Trace Element Sorption by Sediments and Soils - Sites and Processes. In: *Symposium on Molybdenum in the Environment*, W. Chappel, and Petersen, K., eds., M. Dekker, Inc., New York, 425-553.

Jenne, E.A. (ed.) (1979). *Chemical Modeling in Aqueous Systems. Speciation, Sorption, Solubility, and Kinetics*. Symposium Series 93, American Chemical Society, Washington, D.C.

Jones, B.F., Vandenburgh, A.S., Truesdell, A.H., and Rettig, S.L. (1969). Interstitial brines in playa sediments. *Chemical Geology*, **4**, 253-262.

Jones, D.L., and Edwards, A.C. (1993). Effect of moisture content and preparation technique on the composition of soil solution obtained by centrifugation. *Commun. Soil Sci. Plant Anal.*, **24(1-2)**, 171-186.

Jongerius, A., (1957). *Morphologic investigations of soil structure (Morfologische onderzoekingen over de bodemstructuur)*. Bodemkuding Studies n° 2, Mededelingen van Stickting voor Bodemkartering. Wageningen, 93 p.

Jopony, M., and Young, S.D. (1994). The Solid⇌Solution Equilibria of Lead and Cadmium in Polluted Soils. *European Journal of Soil Science*, **45(1)**, 59-70.

Kaback, D.S. (1976). Transport of molybdenum in mountainous stream, Colorado. *Geochimica et Cosmochimica Acta*, **40**, 581-582.

Kabata-Pendias, A., and Pendias, H. (1984). *Trace elments in soils and plants*, CRC Press, Boca Raton, Florida.

Kashem, M.A., and Singh, B.R. (2001). Metal availability in contaminated soils: I. Effects of flooding and organic matter on changes in Eh, pH and solubility of Cd, Ni andZn. *Nutrient Cycling in Agroecosystems*, **61(3)**, 247-255.

Kato, Y., Tanase, M. , Minami, H., and Okabe, S. (1995). Remobilization of transition elements in pore water of continental slope sediments. In: *Biogeochemical Processes and Ocean Flux in the Western Pacific*, H. Sakai, and Nozaki,Y., ed., Terra Scientific Publishing, Tokyo.

Keefer, R.F., Singh, R.N., and Horvath, D.J. (1986). Chemical-composition of vegetables grown on an agricultural soil amended with sewage sludges. *Journal of Environmental Quality*, **15(2)**, 146-152.

Keizer, M.G. (1991). ECOSAT, a computer program for the calculation of speciation in soil-water systems. Department of Soil Science and Plant Nutrition, Agricultural University, Wageningen, The Nederlands.

Keller, C., Kayser, A., Keller, A., and Schulin R. (2001). Heavy metal uptake by agricultural crops from sewage-sludge treated soils from the Upper Swiss Rhine Valley and the effect of time. In: *Environmental restoration of metal-contaminated soils*, I. K. Iskandar, ed., CRC Press LLC, 273-291.

Khasawneh, F.E., and Adams, F. (1967). Effect of dilution on calcium and potassium contents of soil solutions. *Soil Science Society of America Journal*, **31**, 172-176.

Kinniburgh, D.G., and Miles, D.L. (1983). Extraction and chemical analysis of interstitial water from soils and rocks. *Environmental Science and Technology*, **17(6)**, 362-368.

Kinniburgh, D.G., Jackson, M.L., Syers, J.K. (1976). Adsorption of alkaline earth, transition, and heavy metal cations by hydrous oxide gels of iron and aluminium. *Soil Science Society of America Journal*, **40**, 796-799.

Kinniburgh, D.G., Milne, C.J., Benedetti, M.F., Pinheiro, J.P., Filius, J., Koopal, L.K., and VanRiemsdijk, W.H. (1996). Metal ion binding by humic acid: Application of the NICA-Donnan model. *Environmental Science and Technology*, **30(5)**, 1687-1698.

Kinniburgh, D.G., van Riemsdijk, W.H., Koopal, L.K., Borkovec, M., Benedetti, M.F., and Avena, M.J. (1999). Ion binding to natural organic matter: competition, heterogeneity, stoichiometry and thermodynamic consistency. *Colloids and Surfaces – A - Physicochemical and Engineering Aspects*, **151(1-2)**, 147-166.

Knight, B.P., Chaudri, A.M., McGrath, S.P., and Giller, K.E. (1998). Determination of chemical availability of cadmium and zinc in soils using inert soil moisture samplers. *Environmental Pollution*, **99**, 293-298.

Koch, M., and Rotard, W. (2001). On the contribution of background sources to the heavy metal content of municipal sewage sludge. *Water Science and Technology*, **43(2)**, 67-74.

Koch, M., Knoth, W., and Rotard, W. (2001). Source identification of PCDD/Fs in a sewage treatment plant of a German village. *Chemosphere*, **43(4-7)**, 737-741.

Krahn, J., and Fredlund, D.G. (1972). On total, matric and osmotic suction. *Soil Science*, **114(5)**, 339-348.

Krauskopf, K.B. (1995). *Introduction to Geochemistry*, McGraw-Hill Publishing Co., New York.

Kriukov, P.A. (1971). Gornye, pochverrye i Ilovye Rastvory (Interstitial waters of soils, rocks and sediments). *Izdatel, stvo Nauka, Moskow*.

Kuo, S. (1986). Concurrent sorption of phosphate and zinc, cadmium, or calcium by a hydrous ferric oxide. *Soil Science Society of America Journal*, **50**, 1412-1419.

Kutilek, M., and Nielsen, D. (1994). *Soil hydrology*, Catena Verlag.

Lambe, T.W., and Whitman, R.V. (1979). *Soil mechanics, SI Version*, John Wiley & Sons, New York.

Landon, M.K., Delin, G.N., Komor, S.C., and Regan, C.P. (1999). Comparison of the stable-isotopic composition of the soil water collected from suction lysimeters, wick samplers, and cores in a sandy unsaturated zone. *Journal of Hydrology*, **224**, 45-54.

Langenkamp, H., and Marmo, L. (2000). Problems around sludge, Workshop on. *Problems around sludge, Workshop on*, Stresa (NO) Italy.

Langmuir, D. (1997). *Aqueous Environmental Geochemistry*, Prentice Hall, 576 p.

Larsen, S., and Widdowson, A.E. (1968). Chemical composition of soil solution. *Journal of the Science of Food and Agriculture*, **19**, 693-695.

Lee, J.H., and Doolittle, J.J. (2002). A proposed method for determining soil phosphorus desorption quantity-intensity relationships using anion-exchange membrane disks. *Communications in Soil Science and Plant Analysis*, **33(11-12)**, 1941-1958.

Levin, M.J., and Jackson, D.R. (1977). A comparison of in situ extractors for sampling soil water. *Soil Science Society of America Journal*, **41**, 535-536.

Lindroos, A.J., Brugger, T., Derome, J., and Derome, K. (2003). The weathering of mineral soil by natural soil solutions. *Water Air and Soil Pollution*, **149(1-4)**, 269-279.

Lindsay, W.L. (1979). *Chemical equilibria in soils*, John Wiley, New York.

Litaor, M.I. (1988). Review of soil solution samplers. *Water Resources Research*, **24(5)**, 727-733.

Lofts, S., and Tipping, E. (1998). An assemblage model for cation binding by natural particulate matter. *Geochimica et Cosmochimica Acta*, **62(15)**, 2609-2625.

Logan, T.J., Harrison, B.J., McAvoy, D.C., and Greff, J.A. (1996). Effects of olestra in sewage sludge on soil physical properties. *Journal of Environmental Quality*, **25(1)**, 153-161.

Lorenz, S.E., Hamon, R.E., and McGrath, S.P. (1994). Differences between soil solutions obtained from rhizosphere and non-rhizosphere soils by water displacement and soil centrifugation. *European Journal of Soil Science*, **45**, 431-438.

Lumsdon, D.G., and Evans, L.J. (1995). Predicting chemical speciation and computer simulation. In: *Chemical speciation in the environment*, A.M. Ure, and Davidson, C.M., ed., Blackie Academic & Professional, an imprint of Chapman & Hall, Glasgow, 86-134.

Luo, Y.M., Qiao, X. L., Song, J., Christie, P., and Wong, M.H. (2003). Use of a multi-layer column device for study on leachability of nitrate in sludge-amended soils. *Chemosphere*, **52(9)**, 1483-1488.

Luo, Y.M., Yan, W.D., and Christie, P. (2001). Soil solution dynamics of Cu and Zn in a Cu- and Zn-polluted soil as influenced by gamma-irradiation and Cu-Zn interaction. *Chemosphere*, **42(2)**, 179-184.

Luxmoore, R.J. (1981). Micro-, meso- and macroporosity of soil. *Soil Science Society of America Journal*, **45**, 671.

Luxmoore, R.J., Jardine, P.M., Wilson, G.V., Jones, J.R., and Zelazny, L.W. (1990). Physical and chemical controls of preferred path flowthrough a forested hillslope. *Geoderma*, **46**, 139–154.

MAFF, (1994). Fertiliser recommentations for agricultural and horticultural crops. *Reference Book 209, 6th edn.*, Ministry of Agriculture, Fisheries and Food, London.

MAFF, (1996). Information on the application of sewage sludge to agricultural land. *PB2568*, Ministry of Agriculture, Fishieries and Food, London.

MAFF, (1998). Code of good agricultural practice for the protection of soil. Ministry of Agriculture, Fisheries and Food, London.

Magnusson, T. (1992). *Temporal and spatial variation of the soil atmosphere in forest soils of northern Sweden*, Stencil Institutionen for Skoglig Standortoslara, Sveriges Lantbruksuniversitet, Swedish Univ. Agric. Sci., Ume, Sweden.

Manheim, F.T. (1966). A hydraulic squeezer for obtaining interstitial waters from consolidated and unconsolidated sediments. *550-556*, USGS, Washington.

Marinsky, J.A., and Ephraim, J.H. (1986). A unified physicochemical description of the protonation and metal ion complexation equilibria of natural organic acids (humic and fulvic acids) - 1. Analysis of the influence of polyelectrolyte properties on protonation equilibria in ionic media: Fundamental concepts. *Environmental Science and Technology*, **20**, 349-354.

Marshall, T.J. (1959). The diffusion of gases through porous media. *Journal of Soil Science*, **10**, 79-84.

Marshall, T.J., and Holmes, J.W. (1979). *Soil physics*, Cambridge University Press, Cambridge.

Martinez, C.E., and Motto, H.L. (2000). Solubility of lead, zinc and copper added to mineral soils. *Environmental Pollution*, **107**, 153-158.

Masscheleyn, P.H., Delaune, R.D., and Patrick, W.H. Jr. (1991). Effect of redox potential and pH on arsenic speciation and solubility in a contaminated soil. *Environmental Science and Technology*, **25**, 1414-1419.

Massee, R., and Maessen, F.J.M.J. (1981). Losses of silver, arsenic, cadmium, selenium, and zinc traces from distilled water and artificial sea-water by sorption on various container surface. *Analytica Chimica Acta*, **127**, 206-210.

Mattigod, S.V. (1995). Chemical equilibrium and reaction models: applications and future trends. In: *Chemical Equilibrium and Reaction Models*, S. Leoppert R.H., A.P., and Goldberg, S., ed., Soil Science Society of America, special publication 42.

Mattigod, S.V., and Sposito, G. (1979). Chemical modeling of trace metal equilibria in contaminated soil solution using the computer. In: *Chemical modeling in aqueous systems*, E. A. Jenne, ed., American Chemical Society, Washington, 837-856.

Mattigod, S.V., Page, A.L., and Thornton, I. (1986). Identification of some trace element minerals in a mine-waste contaminated soil. *Soil Science Society of America Journal*, **50**, 254-258.

Mattigod, S.V., Sposito, G., and Page, A.L. (1981). Factors affecting the solubilities of trace metals in soils. Chemistry in the soil environment, M. Stelly, ed., American Society of Agronomy - Soil Science Society of America, Madison, WI, 203-221.

Maxted, A.P. (2003). Phytoextraction of cadmium from soils treated with sewage sludge, University of Nottingham, Nottingham.

May, P.M., and Murray, K. (1991a). JESS, A Joint Expert Speciation System, Part I. *Talanta*, **38**, 1409–1417.

May, P.M., and Murray, K. (1991b). JESS, A Joint Expert Speciation System, Part II. *Talanta*, **38**, 1419–1426.

May, P.M., and Murray, K. (1991c). JESS, A Joint Expert Speciation System, Part III. *Talanta*, **38**, 819–825.

Mbila, M.O., Thompson, M.L., Mbagwu, J.S.C., and Laird, D.A. (2001). Distribution and movement of sludge-derived trace metals in selected Nigerian soils. *Journal of Environmental Quality*, **30(5)**, 1667-1674.

McBride, M.B. (1982). Electron-Spin Resonance investigation of Mn^{2+} complexation in natural and synthetic organics. *Soil Science Society of America Journal*, **46(6)**, 1137-1143.

McBride, M.B. (1994). *Environmental chemistry of soils*, Oxford University Press, Inc., New York.

McBride, M.B. (1995). Toxic Metal Accumulation from Agricultural Use of Sludge - Are USEPA Regulations Protective. *Journal of Environmental Quality*, **24(1)**, 5-18.

McBride, M.B. (2003). Toxic metals in sewage sludge-amended soils: has promotion of beneficial use discounted the risks? *Advances in Environmental Research*, **8(1)**, 5-19.

McBride, M.B., and Blasiak, J.J. (1979). Zinc and copper solubility as a function of pH in an acid soil. *Soil Science Society of America Journal*, **43**, 866-870.

McBride, M.B., Richards, B.K., Steenhuis, T., Russo, J.J., and Sauve, S. (1997). Mobility and solubility of toxic metals and nutrients in soil fifteen years after sludge application. *Soil Science*, **162(7)**, 487-500.

McBride, M.B., Sauve, S., and Hendershot, W. (1997). Solubility control of Cu, Zn, Cd and Pb in contaminated soils. *European Journal of Soil Science*, **48(2)**, 337-346.

McGeehan, S.L., and Naylor, D.V. (1994). Sorption and redox transformation of arsenite and arsenate in two flooded soils. *Soil Science Society of America Journal*, **58**, 337-342.

McGrath, S.P. (1995). Chromium and Nickel. In: *Heavy metals in soils*, B.J. Alloway, ed., Blackie Academic & Professional, an imprint of Chapman & Hall, London, 153-178.

McGrath, S.P., and Cegarra, J. (1992). Chemical extractability of heavy metals during and after long-term applications of sewage-sludge to Soil. *Journal of Soil Science*, **43(2)**, 313-321.

McGuire, P.E., Lowery B., Helmke, P.A. (1992). Potential sampling error - Trace metal adsorption on vacuum porous cup samplers. *Soil Science Society of America Journal*, **56(1)**, 74-82.

McHardy, W.J., and Robertson, L. (1983). An optical, scanning electron microscopic and microanalytical study of cementation in some podzol. *Geoderma*, **30**, 161-170.

McKeague, J.A., and Wang, C. (1980). Micromorphology and energy dispersive analysis of orstein horizon pf podzolic soils from New Brunswick and Nova Scotia, Canada. *Canadian Journal of Soil Science*, **60**, 9-21.

Menendez, I., Gallardo, J.F., and Vicente, M.A. (2003). Functional and chemical calibrates of ceramic cup water samplers in forest soils. *Communications in Soil Science and Plant Analysis*, **34(7-8)**, 1153-1175.

Menzies, N.W., and Bell, L.C. (1988). Evaluation of the influence of sample preparation and extraction technique on soil solution composition. *Australian Journal of Soil Research*, **26(3)**, 451-464.

Merrington, G., Oliver, I., Smernik, R.J., and McLaughlin, M.J. (2003). The influence of sewage sludge properties on sludge-borne metal availability.*Advances in Environmental Research*, **8**, 21–36.

Miner, G.S., Gutierrez, R., and King L.D. (1997). Soils factor affecting plant concentrations of cadmium , copper, an zinc on sludge-amended soils. *Journal of Environmental Quality*, **26**, 989-994.

Morel, F.M.M. (1983). *Principles of Aquatic Chemistry*, John Wiley & Sons, New York.

Morford, J.L., and Emerson, S. (1999). The geochemistry of redox sensitive trace metals in sediments. *Geochimica Et Cosmochimica Acta*, **63(11-12)**, 1735-1750.

Morgenstern, N.R., and Balasubramonian, B.I. (1980). Effects of pore fluid on the swelling of clay shale. *Forth International Conference on Expansive Soils*, Denver, 190-205.

Morrison, G.M.P., Batley, G.E., and Florence, T.M. (1989). Metal Speciation and Toxicity. *Chemistry in Britain*, **25(8)**, 791-796.

Morrison, R., and Szecsody, J. (1985). Sleeve and casing lysimeters for soil pore water sampling. *Soil Science*, **139(5)**, 446-451.

Mubarak, A., and Olsen, R.A. (1976). Immiscible displacement of soil solution by centrifugation. *Soil Science Society of America Journal*, **40(2)**, 329-331.

Nagpal, N.K. (1982). Comparison among, and evaluation of, ceramic porous cup soil water samplers for nutrient transport studies. *Canadian Journal of Soil Science*, **62**, 685-694.

Naidu, R., Bolan, N.S., Kookana, R.S., and Tiller, K.G. (1994a). Ionic strength and pH effects on surface charge and Cd sorption characteristics of soils. *Journal of Soil Science*, **45**, 419-429.

Naidu, R., deLacy, N.J., Bolan, N.S., Kookana, R.S., and Tiller, K.G. (1994b). Effect of inorganic ligands on adsorption of cadmium by soils. *15th International Soil Science Society Congress*, Acapulco, Mexico, 190-191.

NEA, (1996). Survey of Thermodynamic and Kinetic Databases. *NEA/NSC/DOC(96)27*, Nuclear Energy Agency, Nuclear Science Committee.

Nielsen, D.R., van Genuchten, M.T. and Biggar, J.W. (1986). Water flow and solute transport processes in the unsaturated zone. *Water Resources Research*, **22**, 89S-108S.

Nriagu, J.O. (1984). Formation and stability of base metal phosphates in soils and sediments. In: *Phosphate minerals*, J. O. Nriagu, and Moore, P.B., ed., Springer Verlag, Berlin, Heidelberg, 318-329.

Nriagu, J.O., and Dell, C.I. (1974). Diagenetic formation of iron phosphates in recent lake sediments. *American Mineralogy*, 59, 934-946.

Nye, P.H., and Tinker, P.B. (1977). *Solute movement in the soil-root system*, University of California Press, Berkeley, CA.

O'Conner, D.J., and Connolly, J.P. (1980). The effect of concentration of adsorbing solids on the partition coefficient. *Water Research*, **14**, 1517-1523.

O'Neill, P. (1995). Arsenic. In: *Heavy metals in soils*, B.J. Alloway, ed., Blackie Academic & Professional, an imprint of Chapman & Hall, London, 105-121.

Onken, B.M., and Hossner, L.R. (1996). Determination of arsenic species in soil solution under flooded conditions. *Soil Science Society of America Journal*, **60**, 1385-1392.

Oscarson, D.W., and Hume, H.B. (1998). Effect of solid:liquid ratio on the sorption of Sr^{2+} and Cs^{+} on bentonite. In: *Adsorption of metals by geomedia*, E. A. Jenne, ed., Academic Press, London, 277-289.

Padilla, I.Y., Yeh, T.C.J., and Conklin, M.H. (1999). The effect of water content on solute transport in unsaturated porous media. *Water Resources Research*, **35(11)**, 3303-3313.

Pankhurst, D.L., and Appelo, C.A.J. (1999). User's guide to PHREEQC (version 2)- A computer program for speciation, batch-reaction, one-

dimensional transport, and inverse geochemical calculations. *Monograph 78*, U.S. Geological Survey.

Papelis, C., Hayes, K.F., and Leckie, J.O. (1988). HYDRAQL: A program for the computation of chemical equilibrium composition of aqueous batch systems including surface complexation modeling of ion adsorption at the oxide/solution interface. *Technical Report No. 306*, Department of Civil Engineering, Stanford University, Stanford, CA.

Parkpian, P., Klankrong, K., DeLaune, R., and Jugsujinda, A. (2002). Metal leachability from sewage sludge-amended Thai soils. *Journal of Environmental Science and Health Part A - Toxic/Hazardous Substances and Environmental Engineering*, **37(5)**, 765-791.

Paterson, E., and Swaffield, R. (1994). X-ray photolelectron spectroscopy. In: *Spectroscopic and chemical determinative methods*, M. J. Wilson, ed., Chapman & Hall, London, 226-259.

Percival, H.J. (2003). Soil and soil solution chemistry of a New Zealand pasture soil amended with heavy metal-containing sewage sludge.*Australian Journal of Soil Research*, **41(1)**, 1-17.

Perdue, E.M., Beck, K.C., and Reuter, J.H. (1976). Organic complexes of iron and aluminum in natural waters. *Nature*, **260**, 418.

Pérez, D.V., De Campos, R.C., and Meneguelli, N.A. (2004). Effects of soil sample storage treatment on the composition and Fe, Al, and Mn speciation of soil solutions obtained by centrifugation. *Water Air and Soil Pollution*, **151(1-4)**, 195-214.

Pérez, D.V., de Campos, R.C., and Novaes, H.B. (2002). Soil solution charge balance for defining the speed and time of centrifugation of two Brazilian soils. *Communications in Soil Science and Plant Analysis*, **33(13-14)**, 2021-2036.

Petruzzelli, G., Guidi, G., and Lubrano, L. (1985). Ionic strength effect on heavy metal adsorption by soil. *Communications in Soil Science and Plant Analysis*, **16**, 971–986.

Phillip, J. (1968). Steady infiltration from buried point sources and spherical cavities. *Water Resources Research*, **4(5)**, 1039-1047.

Pignatello, J.J., and Xing, B. (1996). Mechanisms of slow sorption of organic chemicals to natural particles. *Environmental Science and Technology*, **30(1)**, 1-11.

Polo, M.J., Ordonez, R., and Giraldez, J.V. (1999). Copper and zinc adsorption by sewage sludge-treated soil in Southern Spain. *Communications in Soil Science and Plant Analysis*, **30(7-8)**, 1063-1079.

Pomogailo, A.D., and Wöhrle, D. (1996). Synthesis and structure of macromolecular metal complexes. In: *Macromolecule-metal complexes*, F. Ciardelli, Tsuchida, E., and Wöhrle, D., ed., Springer, Berlin, 11-129.

Prokop, Z., Cupr, P., Zlevorova-Zlamalikova, V., Komarek, J., Dusek, L., and Holoubek, I. (2003). Mobility, bioavailability, and toxic effects of cadmium in soil samples. *Environmental Research*, **91(2)**, 119-126.

Qafoku, N.P., Ainsworth, C.C., Szecsody, J.E., Qafoku, O.S., and Heald, S.M. (2003). Effect of coupled dissolution and redox reactions on Cr(VI)(aq) attenuation during transport in the sediments under hyperalkaline conditions. *Environmental Science and Technology*, **37(16)**, 3640-3646.

Raven, K.P., and Hossner, L.R. (1994). Sorption and Desorption Quantity-Intensity Parameters Related to Plant-Available Soil-Phosphorus. *Soil Science Society of America Journal*, **58(2)**, 405-410.

Rawlins, B.G., O'Donnell, K., and Ingham, M. (2003). Geochemical survey of the Tamar cachment (south-west England). *CR/03/027*, NERC, British Geological Survey, Keyworth, Nottingham.

Reeder, S., Cave, M.R. , Entwisle, D.C., and Trick, J.K. (1998). Extraction of water and solutes from clayey material: a review and critical discussion of available techniques. *WI/98/4C*, British Geological Survey, Keyworth, Nottingham.

Reemtsma, T., Bredow, A., and Gehring, M. (1999). The nature and kinetics of organic matter release from soil by salt solution. *European Journal of Soil Science*, **50**, 53-64.

Reilly, C. (1991). *Metal contamination of food*, Elsevier Applied Science, London and New York.

Reitemeier, R. F. (1946). Effects of moisture content on the dissolved and exchangeable ions of soils of arid regions. *Soil Science*, **61**, 195-214.

Richards, L.A., and Weaver, L.R. (1944). Moisture retention by some irrigated soils as related to soil moisture tension. *Journal of Agricultural Research*, **69**, 215-235.

Richards, P.L., and Kump, L.R. (2003). Soil pore-water distributions and the temperature feedback of weathering in soils. *Geochimica et Cosmochimica Acta*, **67(20)**, 3803-3815.

Robb, F., and Young, S.D. (1999). Addition of calcareous metal wastes to acid soils: consequences for metal solubility. *Water Air and Soil Pollution*, **111(1-4)**, 201-214.

Ross, C.A.M., Bath, A.H., Entwisle, D.C., Cave, M.R., Fry, M.B., Green, K.A. and Reeder, S. (1989). Hydrochemistry of porewaters from Jurassic Oxford Clay, Kellaways Beds, Upper Estuarine and Upper Lias formations at the Elstow site, Bedfordshire. *WE/89/28*, British Geological Survey, Keyworth, Nottingham.

Ross, D.S., and Bartlett, R.J. (1990). Effects of Extraction Methods and Sample Storage on Properties of Solutions Obtained from Forested Spodosols. *Journal of Environmental Quality*, **19(1)**, 108-113.

Ross, S.M. (1996). *Toxic metals in soil-plant system*, John Wiley & Sons, Chichester, West Sussex, England.

Rowell, D.L. (1994). *Soil science: methods and applications*, Longman, Harlow.

Sadiq, M. (1997). Arsenic chemistry in soils: an overview of thermodynamic predictions and field observations. *Water, Air and Soil Pollution*, **93**, 117-136.

Salam, A.K., and Helmke, P.A. (1998). The pH dependence of free ionic activities and total dissolved concentrations of copper and cadmium in soil solution. *Geoderma*, **83(3-4)**, 281-291.

Sanchez-Martin, M.J., and Sanchez-Camazano, M. (1993). Adsorption and mobility of cadmium in natural, uncultivated soils. *Journal of Environmental Quality*, **22**, 737–742.

Sauvé, S., Dumestre, A., McBride, M., and Hendershot, W. (1998). Derivation of soil quality criteria using predicted chemical speciation of Pb^{2+} and Cu^{2+}. *Environmental Toxicology and Chemistry*, **17(8)**, 1481-1489.

Sauvé, S., Hendershot, W., and Allen, H.E. (2000). Solid-solution partitioning of metals in contaminated soils: Dependence on pH, total metal burden, and organic matter. *Environmental Science and Technology*, **34(7)**, 1125-1131.

Senesi, N. (1992). Binding Mechanisms of Pesticides to Soil Humic Substances. *Science of the Total Environment*, **123**, 63-76.

Scheckel, K.G., and Sparks, D.L. (2001). Temperature effects on nickel sorption kinetics at the mineral-water interface. *Soil Science Society of America Journal*, **65**, 719-728.

Schnitzer, M. (1978). Humic substances: chemistry and reactions. In: *Soil Organic Matter*, M. Schnitzer, and Khan, S.U. (eds), ed., Elsevier, Amsterdam, pp. 1–64.

Schofield, R.K. (1947). A ratio law governing the equilibrium of cations in the soil solution. *11th International Congress of Pure Applied Chemistry*, London, 257-261.

Schubert, H. (1982). *Kapillarität in porösen feststoffsystemen*, Springer-Verlag, Berlin.

Shaffer, R.J., Wallace, J., and Garwood, F. (1937). The centrifuge method of investigating the variation of hydrostatic pressure with water content in porous material. *Transactions of the Faraday Society*, **33**, 723-734.

Shan, X.Q., Wang, Z.W., Wang, W.S., Zhang, S.Z., and Wen, B. (2003). Labile rhizosphere soil solution fraction for prediction of bioavailability of heavy metals and rare earth elements to plants. *Analytical and Bioanalytical Chemistry*, **375(5)**, 400-407.

Shaw, E.M. (1993). *Hydrology in practice*, Chapman & Hall, London.

Shaw, T.J., Gieskes, J.M., and Jahnke, R.A. (1990). Early diagenesis in differing depositional environments: The response of transition metals in pore water. *Geochimica et Cosmochimica Acta*, **54**, 1233-1246.

Shendrikar, A.D., Dharmarajan, V., Walker-Merrick, H., and West, P.W. (1975). Adsorption characteristics of traces of barium, beryllium, cadmium, manganese, lead, and zinc on selected surfaces. *Analytica Chimica Acta*, **84**, 409/417.

Sheppard, M.I., Thibault, D.H., and Smith, P.A. (1992). Effect of extraction techniques on soil pore-water chemistry. *Communications in Soil Science and Plant Analysis*, **23(13-14)**, 1643-1662.

Sholkovits, E. (1973). Interstitial water chemistry of the Santa Barbara basin sediments. *Geochimica et Cosmochimica Acta*, **37**, 2043-2078.

Siemens, J., and Kaupenjohann, M. (2003). Dissolved organic carbon is released from sealings and glues of pore-water samplers. *Soil Science Society of America Journal*, **67(3)**, 795-797.

Sillen, L. G. (1967). Master variables and activity scales. Equilibrium concepts in natural-water systems, American Chemical Society, Washington, DC.

Sills, I.D., Aylmore, L.A.G., and Quirk, J.P. (1974). Relationship between pore size distribution and physical properties of a clay soil. *Australian Journal of Soil Research*, **12**, 107-117.

Simkiss, K., and Taylor, M.G. (1989). Metal fluxes across membranes of aquatic organisms. *Reviews in Aquatic Science*, **1**, 174-188.

Snyder, R.L., and Bish, D.L. (1989). Quantitative analysis (Chapter 5). In: *Modern Powder Diffraction*, D. L. Bish, Post, J.E. (Eds), ed., Mineralogical Society of America, USA, 101-144.

Sonesson, U., Bjorklund, A., Carlsson, M., and Dalemo, M. (2000). Environmental and economic analysis of management systems for biodegradable waste. *Resources Conservation and Recycling*, **28(1-2)**, 29-53.

Sörme, L., and Lagerkvist, R. (2002). Sources of heavy metals in urban wastewater in Stockholm. *Science of the Total Environment*, **298(1-3)**, 131-145.

Sort, X., and Alcaniz, J.M. (1999). Modification of soil porosity after application of sewage sludge. *Soil & Tillage Research*, **49(4)**, 337-345.

Spangenberg, A., Cecchini, G., and Lamesdorf, N. (1997). Analysing the preformance of a micro soil solution sampling device in a laboratory examination and a field experiment. *Plant and Soil*, **196**, 59-70.

Sparks, D.L. (1995). *Environmental soil chemistry*, Acedemic Press, Inc., San Diego, CA.

Sposito, G. (1984). *The surface chemistry of soils*, Oxford University Press, New York.

Sposito, G. (1989). *The chemistry of soils*, Oxford University Press, New York.

Sposito, G., and Coves, J. (1988). SOILCHEM: A computer program for the calculation of chemical speciation in soils. The Kearney Foundation of Soil Science, University of California, Riverside and Berkeley, CA.

Sterrett, S.B., Chaney, R.L., Gifford, C.H., and Mielke, H.W. (1996). Influence of fertilizer and sewage sludge compost on yield and heavy metal accumulation by lettuce grown in urban soils. *Environmental Geochemistry and Health*, **18(4)**, 135-142.

Stevenson, F.J. (1987). Geochemistry of soil humic substances. In: *Humic substances in soil*, sediment and water, G. Aiken, McKnight, D.M., Wershaw, R.L., and MacCarthy, P., ed., John Wiley & Sons, New York, 13-52.

Stevenson, F.J., and Fitch, A. (1986). Chemistry of complexation of metal ions with soil solution organics. In: *Interactions of soil minerals with natural organics and microbes*, Huang, ed., ASA and SSSA, Madison, WI, p. 29–58.

Stewart, G.L. (1972). Clay-water interaction, the behaviour of ^{3}H and ^{2}H in adsorbed water, and the isotope effect. *Soil Science Society of America Proceedings*, **36**, 421-426.

Stumm, W., and Morgan, J.J. (1996). *Aquatic chemistry, chemical equilibria and rates in natural waters*, 3rd Edition, John Wiley & Sons, Inc., New York, p. 1022.

Suarez, D.L., and Goldberg, S. (1994). Modeling soil solution, mineral formation and weathering. In: *Quantitative modeling of soil forming processes*, R. B. Bryant, and Arnold, R. W., ed., Soil Science Society of America, Madison, 37-60.

Sutherland, R.A. (1998). Loss-on-ignition estimates of organic matter and relationships to organic carbon in fluvial bed sediments. *Hydrobiologia*, **389**, 153-167.

Swanson, K.A., and Johnson, A.H. (1980). Trace metal budgets for a forested watershed in the New Jersey Pine Barrens. *Water Resources Research*, **16**, 373.

Tack, F.M.G., and Verloo, M.G. (1995). Chemical speciation and fractionation in soil and sediment heavy metal analysis: a review. *International Journal of Environmental Analytical Chemistry*, **59(2-4)**, 225.

Talibudeen, O. (1981). Cation exchange in soil. In: *The chemistry of soil processes*, Greenland D.J., and Hayes M.H.B., ed., Wiley & Sons Ltd, Chichester and New York, 115-177.

Tan, T.C., and Teo, W.K. (1987). Combined effect of carbon dosage and initial adsorbate concentration on the adsorption isotherm of heavy metals on activated carbon. *Water Research*, **21**, 1183-1188.

Tang, K.L., and Feng, X.H. (2001). The effect of soil hydrology on the oxygen and hydrogen isotopic compositions of plants' source water. *Earth and Planetary Science Letters*, **185(3-4)**, 355-367.

Taylor, R.M., and Giles, J.B. (1970). Association of Vanadium and Molybdenum with Iron Oxides in Soils. *Journal of Soil Science*, **21(2)**, 203.

Templeton, G.D., and Chasteen, N.D. (1980). Vanadium-Fulvic Acid Chemistry - Conformational and Binding- Studies by Electron-Spin Probe Techniques. *Geochimica Et Cosmochimica Acta*, **44(5)**, 741-752.

Tessier, A., Campbell, P.G.C., and Bisson, M. (1979). Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry*, **51**, 844-851.

Theng, B.K.G. (1979). *Formation and properties of clay-polymer complexes*, Elsevier, Amsterdam.

Thornton, I. (1983). Geochemistry applied to agriculture. In: *Applied environmental geochemistry*, I. Thornton, ed., Academic Press, London, 231-266.

Thurman, E.M. (1985). *Organic Geochemistry of Natural Waters*, Nijhoff-Junk, Dordrecht.

Tiensing, T., Preston, S., Strachan, N., and Paton, G.I. (2001). Soil solution extraction techniques for microbial ecotoxicity testing: a comparative evaluation. *Journal of Environmental Monitoring*, **3(1)**, 91-96.

Tiller, K.G. (1989). Heavy metals in soils and their environmental significance. *Advances in Soil Science*, **9**, 113-142.

Tiller, K.G., Hogson, J.F., Peech, M. (1963). Specific sorption of cobalt by soil clays. *Soil Sciences*, **15**, 392-399.

Tipping, E. (1994). WHAM - a chemical-equilibrium model and computer code for waters, sediments, and soils incorporating a discrete site electrostatic model of ion-binding by humic substances. *Computers & Geosciences*, **20(6)**, 973-1023.

Tipping, E. (1998). Humic ion-binding model VI: An improved description of the interactions of protons and metal ions with humic substances. *Aquatic Geochemistry*, **4(1)**, 3-48.

Tipping, E. (2002). *Cation binding by humic substances*, Cambridge University Press, Cambridge.

Tipping, E., and Hurley, M.A. (1992). A unifying model of cation binding by humic substances. *Geochimica et Cosmochimica Acta*, **56(10)**, 3627-3641.

Tipping, E., Reddy, M.M., and Hurley, M.A. (1990). Modeling electrostatic and heterogeneity effects on proton dissociation from humic substances. *Environmental Science and Technology*, **24(11)**, 1700-1705.

Town, R.M., and Filella, M. (2002). Implications of natural organic matter binding heterogeneity on understanding lead(II) complexation in aquatic systems. *The Science of the Total Environment*, **300**, 143-154.

Truesdell, A., and Jones, B.F. (1974). WATEQ, A computer program for calculating chemical equilibria of natural waters. *Journal of Research, U.S. Geol. Survey*, **2(2)**, 233-248.

Tuck, J.J., Hall, P.L., Hayes, M.H.B., Ross, D.K., and Hayter, J.B. (1985). Quasi-Elastic Neutron-Scattering studies of intercalated molecules in charge-deficient layer silicates. 2. High-resolution measurements of the diffusion of water in montmorillonite and vermiculite. *Journal of the Chemical Society-Faraday Transactions I*, **81**, 833-846.

Turner, R.S., Wang, D.W., and Johnson, A.H. (1985). Biogeochemistry of lead in McDonald's Branch Watershed, New Jersey Pine Barrens. *Journal of Environmental Quality*, **14**, 305.

Tye, A.M., Young, S.D., Crout, N.M.J., Zhang, H., Preston, S., Barbosa-Jefferson, V.L., Davison, W., McGrath, S.P., Paton, G.I., Kilham, K., and Resende, L. (2003). Predicting the activity of Cd^{2+} and Zn^{2+} in soil pore water from the radio-labile metal fraction. *Geochimica et Cosmochimica Acta*, **67(3)**, 375-385.

Tye, A.M., Young, S.D., Crout, N.M.J., Zhang, H., Preston, S., Bailey, E.H., Davison, W., McGrath, S.P., Paton, G.I., and Kilham, K. (2002). Predicting arsenic solubility in contaminated soils using isotopic dilution techniques. *Environmental Science and Technology*, **36(5)**, 982-988.

Tyler, G. (2000). Effects of sample pretreatment and sequential fractionation by centrifuge drainage on concentrations of minerals in a calcareous soil solution. *Geoderma*, **94**, 59-70.

United Nations General Aassembly, (1996). IV. State of the Antartic environment: Synopsis of some recent findings, available online at: http://www.gridc.canterbury.ac.nz/unga

Van Benschoten, J.E., Young, W.H., Matsumoto, M.R., and Reed, B.E. (1998). A nonelectrostatic surface complexation model for lead sorption on soils and mineral surfaces. *Journal of Environmental Quality*, **27**, 24-30.

Van Genuchten, M.T., and Wierenga, P.J. (1976). Mass transfer studies in sorbing porous media. I. Analytical solutions. *Soil Science Society of America Journal*, **40**, 473-480.

Vempati, R.K., Hess, T.R., and Cocke, D.L. (1996). X-ray photoelectron spectroscopy. In: *Methods of Soil Analysis, Part 3 - Chemical Methods*, D. L. Sparks, ed., Soil Science Society of America, Madison, WI, 357-375.

Vig, K., Megharaj, M., Sethunathan, N., and Naidu, R. (2003). Bioavailability and toxicity of cadmium to microorganisms and their activities in soil: a review. *Advances in Environmental Research*, **8(1)**, 121-135.

Vlek, P.L.G., and Lindsay, W.L. (1977). Thermodynamic stability and solubility of molybdenum minerals in soil. *Soil Science Society of America Journal*, **41**, 42-46.

Voice, T.C., and Weber, J.W.J. (1985). Sorbent concentration effects in liquid/solid partitioning. *Environmental Science and Technology*, **19**, 789-796.

Voice, T.C., Rice, C.P., and Weber, J.W.J. (1983). Effects of solids concentration on the sorptive partitioning of hydrophobic pollutants in aquatic systems. *Environmental Science and Technology*, **17**, 513-518.

Walker, G.R., Woods, P.H., and Allison, G.B. (1994). Interlaboratory comparison of methods to determine the stable- isotope composition of soil-water. *Chemical Geology*, **111(1-4)**, 297-306.

Warren, L.A., and Haack, E.A. (2001). Biogeochemical controls on metal behaviour in freshwater environments. *Earth-Science Reviews*, **54(4)**, 261-320.

Warrick, A.W., and Amoozegar-Fard, A. (1977). Soil-water regimes near porous cup water samplers. Water Resources Research, **13(1)**, 203-207.

Warwick, P., Hall, A., and Read, D. (1994). A comparative-study employing 3 different models to investigate the complexation properties of humic-acid and fulvic-acid. *Radiochimica Acta*, **66-7**, 133-140.

Washburn, E.W. (1921). The Dynamics of Capillary Flow. *The American Physical Society, 2nd series*, 17, 374-375.

Webber, M.D., and Bedford, J.A. (1996). Organic and Metal contaminants in Canadian Municipal Sludges and a Sludge Compost: Supplemental Report. *1996-RES-3*, WTI, Burlington, Ontario.

Webber, M.D., and Nichols, J. (1995). Organic and Metal Contaminants in Canadian Municipal Sludges and a Sludge Compost: Wastewater Technology Centre. WTI, Burlington, Ontario.

Wehrli, B., and Stumm, W. (1989). Vanadyl in Natural-Waters - Adsorption and Hydrolysis Promote Oxygenation. *Geochimica Et Cosmochimica Acta*, **53(1)**, 69-77.

Welp, G., and Brummer, G.W. (1999). Adsorption and solubility of ten metals in soil samples of different composition. *Journal of Plant Nutrition and Soil Science-Zeitschrift Fur Pflanzenernahrung Und Bodenkunde*, **162(2)**, 155-161.

Weng, L.P., Temminghoff, E.J.M., Lofts, S., Tipping, E., and Van Riemdijk, W.H. (2002). Complexation with dissolved organic matter and solubility

control of heavy metals in a sandy soil. *Environmental Science and Technology*, **36(22)**, 4804-4810.

Wenzel, W.W., and Wieshammer, G. (1995). Suction cup materials and their potential to bias trace-metal analyses of soil solutions - a review. *International Journal of Environmental Analytical Chemistry*, **59(2-4)**, 277-290.

Wenzel, W.W., Sletten, R.S., Brandstetter, A., Wieshammer, G., and Stingeder, G. (1997). Adsorption of trace metals by tension lysimeters: Nylon membrane vs. porous ceramic cup. *Journal of Environmental Quality*, **26(5)**, 1430-1434.

Wheatstone, K.C., and Gelsthorpe, D. (1982). Extraction and analysis of interstitial water from sandstone. *Analyst*, **107**, 731-736.

Whelan, B.R., and Barrow, N.J. (1980). A study of a method for displacing soil solution by centrifuging with an immiscible liquid. *Journal of Environmental Quality*, **9(2)**, 315-319.

White, R.E. (1985). The influence of macropores on the transport of dissolved and suspended matter through soil. *Advances in Soil Science*, **3**, 95-120.

White, R.E. (1987). *Introduction to the Principles and Practice of Soil Science*, Blackwell Scientific, Oxford.

Wiersum, L.K. (1957). The relationship of the size and structural rigidity of pores to their penetration by roots. *Plant and Soil*, **9**, 75-85.

Wilson, S. C., Alcock, R.E., Sewart, A.P., and Jones, K.C. (1997). Persistence of organic contaminants in sewage sludge-amended soil: A field experiment. *Journal of Environmental Quality*, **26(6)**, 1467-1477.

Wolery, T.J. (1979). Calculation of chemical equilibrium between aqueous solutions and minerals: the EQ3/6 software package. *UCRL-52658*, Lawrence Livermore National Laboratory, Livermore, CA.

Wolt, J. (1994). *Soil solution chemistry: applications to environmental science and agriculture*, John Wiley & Sons, New York.

Yaron, B., Calvet, R., and Prost, R. (1996). *Soil pollution - Processes and Dynamics*, Springer - Verlag, Berlin.

You, S.-J., Yin, Y., and Allen, H.E. (1999). Partitioning of organic matter in soils: effect of pH and water/soil ratio. *The Science of the Total Environment*, **227**, 155-160.

Young, S.D., Tye, A., Carstensen, A., Resende, L., and Crout, N. (2000). Methods for determining labile cadmium and zinc in soil. *European Journal of Soil Science*, **51(1)**, 129-136.

Yuan, G.D., Soma, M., Seyama, H., Theng, B.K.G., Lavkulich, L.M., and Takamatsu, T. (1998). Assessing the surface composition of soil particles from some Podzolic soils by X-ray photolelectron spectroscopy. *Geoderma*, **86**, 169-181.

Zabowski, D. (1989). Limited release of soluble organics from roots during the centrifugal extraction of soil solution. *Soil Science Society of America Journal*, **53(3)**, 977-979.

Zabowsky, D., and Ugolini, F.C. (1990). Lysimeter and centrifuge soil solutions: Seasonal differences between methods. *Soil Science Society of America Journal*, **54**, 1130-1135.

Zachara, J.M., Ainsworth, C.C., Cowan, C.E., and Resch, C.T. (1989). Adsorption of chromate by subsurface soil horizons. *Soil Science Society of America Journal*, **53**, 418–428.

Zhu, C., and Anderson, G. (2002). *Environmental applications of geochemical modeling*, Cambridge University Press, Cambridge.

Ziper, C., Komarneni, S., Baker, D.E. (1988). Specific cadmium sorption in relation to the crystal of clay minerals. *Soil Science Society of America Journal*, **52**, 49-53.